

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**





(19)

(11) Publication number:

**1**

Generated Document.

**PATENT ABSTRACTS OF JAPAN**(21) Application number: **10106014**(51) Intl. Cl.: **C08G 77/14 H01B 1/12**(22) Application date: **16.04.98**

<p>(30) Priority:</p> <p>(43) Date of application publication: <b>02.11.99</b></p> <p>(84) Designated contracting states:</p>	<p>(71) Applicant: <b>KANEGAFUCHI CHEM. LTD</b></p> <p>(72) Inventor: <b>OKADA KENJI</b></p> <p>(74) Representative:</p>
---	--

**(54) POLYSILOXANE  
HAVING CYCLIC  
CARBONATE GROUP ON  
SIDE CHAIN AND ITS  
PRODUCTION**

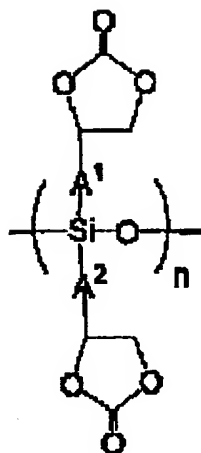
(57) Abstract:

**PROBLEM TO BE SOLVED:** To efficiently obtain a polysiloxane having a substituent group containing a cyclic carbonate on the silicon and useful for polymer solid electrolyte, or the like, usable for battery, or the like.

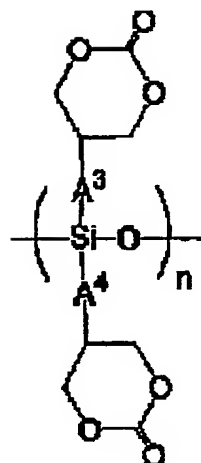
**SOLUTION:** This polysiloxane has two substituent groups each containing a cyclic carbonate on their each silicon and preferably contains siloxane unit. The main chain is preferably represented by formula I [A1 and A2 are each an alkyl, an aryl or the like; (n) is an integer of  $\geq 1$ ], formula II [A3 and A4 are each an alkyl, an aryl or the like] or the like. The polysiloxane is obtained by reacting 1 mol dichlorosilane derivative of formula III (X1 and X2

are each a cyclic carbonate) with preferably 0.5-4.0 mol zinc oxide, preferably in the presence of an organic solvent, preferably at 50-150° C, adding water and a protonic acid to the resultant reaction mixture and stirring these components to produce a diorganopolysiloxane having silanol groups at both ends of molecular chain and subjecting the diorganopolysiloxane to polycondensation in the presence of an acidic condensation catalyst, preferably at 10-150°C.

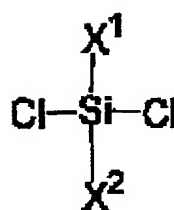
COPYRIGHT: (C)1999,JPO



**I**



## II



11

**(書誌+要約+請求の範囲)**

- (19)【発行国】日本国特許庁(JP).  
 (12)【公報種別】公開特許公報(A).  
 (11)【公開番号】特開平11-302383.  
 (43)【公開日】平成11年(1999)11月2日.  
 (54)【発明の名称】環状カーボネート基を側鎖に有するポリシロキサン及びその製造方法  
 (51)【国際特許分類第6版】

C08G 77/14  
 H01B 1/12  
 // H01M 6/18  
 10/40

**【FI】**

C08G 77/14  
 H01B 1/12       Z  
 H01M 6/18       E  
 10/40            B

**【審査請求】未請求****【請求項の数】9****【出願形態】OL****【全頁数】9**

(21)【出願番号】特願平10-106014

(22)【出願日】平成10年(1998)4月16日

(71)【出願人】

**【識別番号】000000941****【氏名又は名称】鐘淵化学工業株式会社****【住所又は居所】大阪府大阪市北区中之島3丁目2番4号**

(72)【発明者】

**【氏名】岡田 賢治****【住所又は居所】兵庫県神戸市兵庫区吉田町1-2-80鐘淵化学工業株式会社神戸研究所内****(57)【要約】**

**【課題】**低温におけるイオン伝導度、強度などに優れた、各けい素上に環状カーボネートを含有する置換基を2つ有する新規なポリシロキサンを提供する。

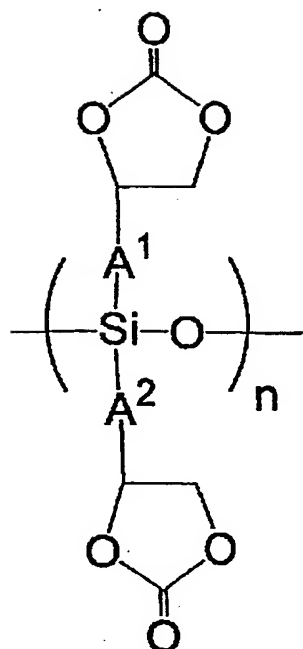
**【解決手段】**ジクロロシランに対し、環状カーボネート構造を有する末端ビニル化合物を白金化合物触媒によりヒドロシリル化させ、得られたジクロロシラン誘導体を縮合重合させることにより各けい素上に環状カーボネートを含有する置換基を2つ有する新規なポリシロキサンを得る。

**【特許請求の範囲】**

**【請求項1】**各ケイ素上に環状カーボネートを含有する置換基を2つ有するポリシロキサン。

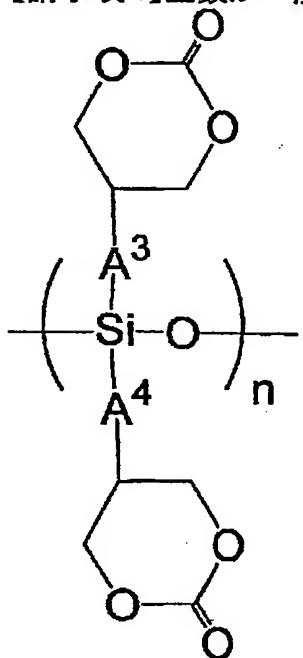
**【請求項2】**各ケイ素上に環状カーボネートを含有する置換基を2つ有するシロキサン単位を含むポリシロキサン。

**【請求項3】**主鎖が一般式【化1】



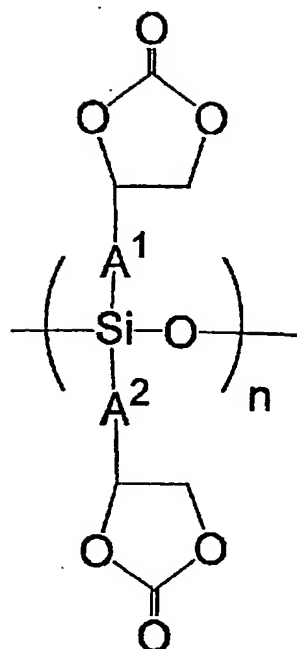
で示される、各ケイ素上に環状カーボネートを含む置換基を2つ有する請求項1に記載のポリシロキサン。(式中A<sup>1</sup>、A<sup>2</sup>は、置換または非置換のアルキル基、アリール基、またはオキシアルキレン基を、nは1以上の整数を表す)。

【請求項4】主鎖が一般式【化2】



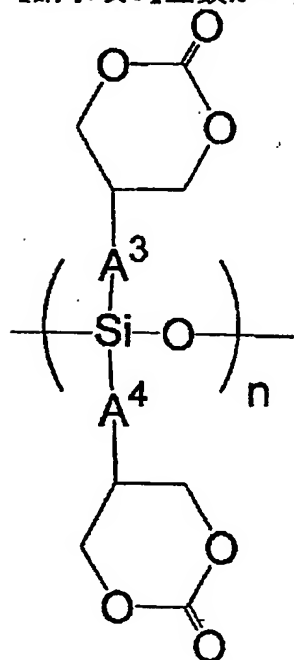
で示される、各ケイ素上に環状カーボネートを含む置換基を2つ有する請求項1に記載のポリシロキサン。(式中A<sup>3</sup>、A<sup>4</sup>は、置換または非置換のアルキル基、アリール基、またはオキシアルキレン基を、nは1以上の整数を表す)。

【請求項5】主鎖が一般式【化3】



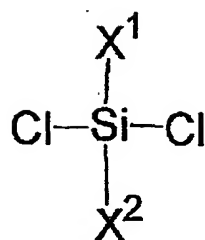
で示される、各ケイ素上に環状カーボネートを含む置換基を2つ有するシロキサン単位を含む請求項2に記載のポリシロキサン。(式中A<sup>1</sup>、A<sup>2</sup>は、置換または非置換のアルキル基、アリール基、またはオキシアルキレン基を、nは1以上の整数を表す)

【請求項6】主鎖が一般式【化4】

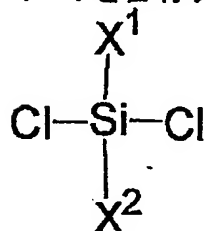


で示される、各ケイ素上に環状カーボネートを含む置換基を2つ有するシロキサン単位を含む請求項2に記載のポリシロキサン。(式中A<sup>3</sup>、A<sup>4</sup>は、置換または非置換のアルキル基、アリール基、またはオキシアルキレン基を、nは1以上の整数を表す)

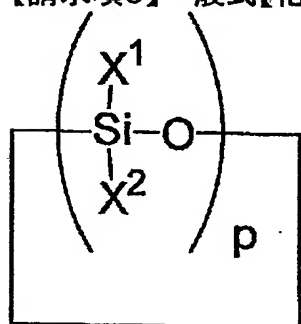
【請求項7】一般式【化5】



(式中 $X^1$ 、 $X^2$ は環状のカーボネート基を有する置換基であり、 $X^1$ 、 $X^2$ はそれぞれ同種または異種であってもよい)で示されるジクロロシラン誘導体と、酸化亜鉛を有機溶媒の存在下で反応させ、次いで、得られた反応混合物に水およびプロトン酸を加えて攪拌することにより、分子鎖両末端にシラノール基を有するジオルガノポリシロキサンを生成せしめ、しかる後に、該ジオルガノポリシロキサンを酸性縮合触媒の存在下に縮合重合させることを特徴とする、請求項1に記載の各けい素上に環状カーボネート基を含有する置換基を2個有するポリシロキサンの製造方法【請求項8】一般式【化6】



(式中 $X^1$ 、 $X^2$ は環状のカーボネート基を有する置換基であり、 $X^1$ 、 $X^2$ はそれぞれ同種または異種であってもよい)で示されるジクロロシラン誘導体を、酸を触媒として溶媒の存在下に混合することにより分子鎖両末端にシラノール基を有するジオルガノポリシロキサンを生成せしめ、しかる後に、該ジオルガノポリシロキサンを酸性縮合触媒の存在下に縮合重合させることを特徴とする、請求項1に記載の各けい素上に置換基として環状カーボネート基を2個有するポリシロキサンの製造方法。【請求項9】一般式【化7】



(式中 $X^1$ 、 $X^2$ は環状のカーボネート基を有する置換基であり、 $X^1$ 、 $X^2$ はそれぞれ同種または異種であってもよく、 $p$ は3または4)で示されるシクロシロキサン誘導体を、プロトン酸触媒の存在下に重合させることを特徴とする、請求項1に記載の各けい素上に置換基として環状カーボネート基を2個有するポリシロキサンの製造方法。



## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-302383

(43)Date of publication of application : 02. 11. 1999

(51)Int. CI.

C08G 77/14  
H01B 1/12  
// H01M 6/18  
H01M 10/40

(21)Application number : 10-106014

(71)Applicant : KANEGAFUCHI CHEM IND CO LTD

(22)Date of filing : 16. 04. 1998

(72)Inventor : OKADA KENJI

## (54) POLYSILOXANE HAVING CYCLIC CARBONATE GROUP ON SIDE CHAIN AND ITS PRODUCTION

## (57)Abstract:

PROBLEM TO BE SOLVED: To efficiently obtain a polysiloxane having a substituent group containing a cyclic carbonate on the silicon and useful for polymer solid electrolyte, or the like, usable for battery, or the like.

SOLUTION: This polysiloxane has two substituent groups each containing a cyclic carbonate on their each silicon and preferably contains siloxane unit. The main chain is preferably represented by formula I [A1 and A2 are each an alkyl, an aryl or the like; (n) is an integer of  $\geq 1$ ], formula II [A3 and A4 are each an alkyl, an aryl or the like] or the like. The polysiloxane is obtained by reacting 1 mol dichlorosilane derivative of formula III (X1 and X2 are each a cyclic carbonate) with preferably 0.5-4.0 mol zinc oxide, preferably in the presence of an organic solvent, preferably at 50-150°C, adding water and a protonic acid to the resultant reaction mixture and stirring these

components to produce a diorganopolysiloxane having silanol groups at both ends of molecular chain and subjecting the diorganopolysiloxane to polycondensation in the presence of an acidic condensation catalyst, preferably at 10-150°C.



I



II



III

## LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision  
of rejection][Kind of final disposal of application  
other than the examiner's decision of  
rejection or application converted]

registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's  
decision of rejection]

[Date of requesting appeal against  
examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998, 2003 Japan Patent Office

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平11-302383

(43) 公開日 平成11年(1999)11月2日

(51) Int. Cl.<sup>6</sup>

識別記号

P I

C 0 8 G 77/14

C 0 8 G 77/14

H 0 1 B 1/12

H 0 1 B 1/12

Z

// H 0 1 M 6/18

H 0 1 M 6/18

E

10/40

10/40

B

審査請求 未請求 請求項の数9 OL (全 9 頁)

(21) 出願番号

特願平10-106014

(22) 出願日

平成10年(1998)4月16日

(71) 出願人 000000941

釜淵化学工業株式会社

大阪府大阪市北区中之島3丁目2番4号

(72) 発明者 岡田 賢治

兵庫県神戸市兵庫区吉田町1-2-80 釜淵

化学工業株式会社神戸研究所内

(54) 【発明の名称】 環状カーボネート基を側鎖に有するポリシロキサン及びその製造方法

(57) 【要約】

【課題】 低温におけるイオン伝導度、強度などに優れた、各けい素上に環状カーボネートを含有する置換基を2つ有する新規なポリシロキサンを提供する。

【解決手段】 ジクロロシランに対し、環状カーボネート構造を有する末端ビニル化合物を白金化合物触媒によりヒドロシリル化させ、得られたジクロロシラン誘導体を縮合重合させることにより各けい素上に環状カーボネートを含有する置換基を2つ有する新規なポリシロキサンを得る。

(2)

特開平11-302383

1

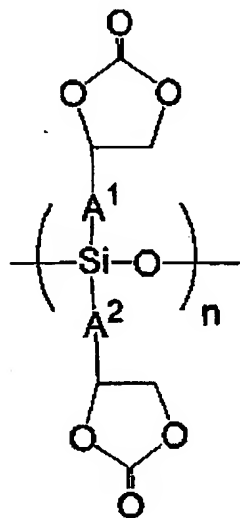
【特許請求の範囲】

【請求項1】各ケイ素上に環状カーボネートを含む置換基を2つ有するポリシロキサン。

【請求項2】各ケイ素上に環状カーボネートを含む置換基を2つ有するシロキサン単位を含むポリシロキサン。

【請求項3】主鎖が一般式

【化1】

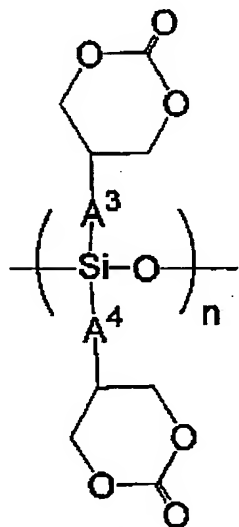


で示される、各ケイ素上に環状カーボネートを含む置換基を2つ有する請求項1に記載のポリシロキサン。

(式中A<sup>1</sup>、A<sup>2</sup>は、置換または非置換のアルキル基、アリール基、またはオキシアルキレン基を、nは1以上の整数を表す)

【請求項4】主鎖が一般式

【化2】



で示される、各ケイ素上に環状カーボネートを含む

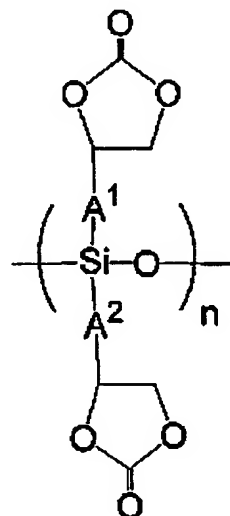
2

置換基を2つ有する請求項1に記載のポリシロキサン。

(式中A<sup>1</sup>、A<sup>2</sup>は、置換または非置換のアルキル基、アリール基、またはオキシアルキレン基を、nは1以上の整数を表す)

【請求項5】主鎖が一般式

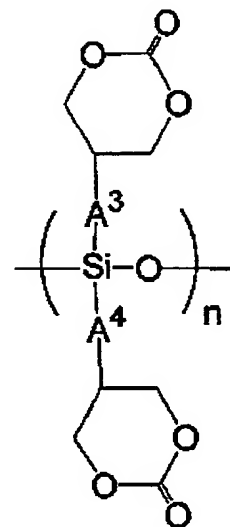
【化3】



で示される、各ケイ素上に環状カーボネートを含む置換基を2つ有するシロキサン単位を含む請求項2に記載のポリシロキサン。(式中A<sup>1</sup>、A<sup>2</sup>は、置換または非置換のアルキル基、アリール基、またはオキシアルキレン基を、nは1以上の整数を表す)

【請求項6】主鎖が一般式

【化4】



で示される、各ケイ素上に環状カーボネートを含む置換基を2つ有するシロキサン単位を含む請求項2に記載のポリシロキサン。(式中A<sup>3</sup>、A<sup>4</sup>は、置換または

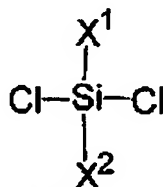
(3)

特開平11-302383

は非置換のアルキル基、アリアル基、またはオキシアルキレン基を、 $n$ は1以上の整数を表す)

【請求項7】一般式

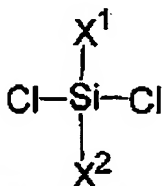
【化5】



(式中 $X^1$ 、 $X^2$ は環状のカーボネート基を有する置換基であり、 $X^1$ 、 $X^2$ はそれぞれ同種または異種であってもよい)で示されるジクロロシラン誘導体と、酸化亜鉛を有機溶媒の存在下で反応させ、次いで、得られた反応混合物に水およびプロトン酸を加えて攪拌することにより、分子鎖両末端にシラノール基を有するジオルガノポリシロキサンを生成せしめ、しかる後に、該ジオルガノポリシロキサンを酸性縮合触媒の存在下に縮合重合させることを特徴とする、請求項1に記載の各けい素上に環状カーボネートを含有する置換基を2個有するポリシロキサンの製造方法

【請求項8】一般式

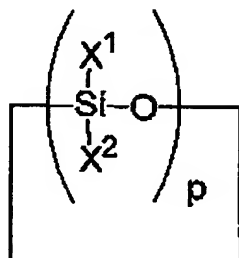
【化6】



(式中 $X^1$ 、 $X^2$ は環状のカーボネート基を有する置換基であり、 $X^1$ 、 $X^2$ はそれぞれ同種または異種であってもよい)で示されるジクロロシラン誘導体を、酸を触媒として溶媒の存在下に混合することにより分子鎖両末端にシラノール基を有するジオルガノポリシロキサンを生成せしめ、しかる後に、該ジオルガノポリシロキサンを酸性縮合触媒の存在下に縮合重合させることを特徴とする、請求項1に記載の各けい素上に置換基として環状カーボネート基を2個有するポリシロキサンの製造方法。

【請求項9】一般式

【化7】



(式中 $X^1$ 、 $X^2$ は環状のカーボネート基を有する置換基

であり、 $X^1$ 、 $X^2$ はそれぞれ同種または異種であってもよく、 $p$ は3または4)で示されるシクロシロキサン誘導体を、プロトン酸触媒の存在下に重合させることを特徴とする、請求項1に記載の各けい素上に置換基として環状カーボネート基を2個有するポリシロキサンの製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は電池などに使用可能な高分子固体電解質などになりうる各けい素上に環状カーボネートを含有する置換基を2つ有するポリシロキサンおよびその製造方法に関する。

【0002】

【従来の技術】近年、樹脂工業が発展するとともに、特殊な性質を有する樹脂が必要になり、それに伴って従来になかった高分子の開発が望まれるようになってきた。エポキシ化合物の開環重合により得られるポリエーテルは、特殊ゴム、界面活性剤など、その用途は広い。またポリエチレンオキドを側鎖に持つ高分子は、リチウム塩などのアルカリ金属塩を可溶化することができ、高分子電解質への研究が盛んである。しかしながら、ポリエチレンオキドはその高い結晶性のために、金属塩の移動度を十分に向上させることができない。

【0003】

【発明が解決しようとする課題】本発明は、各けい素上に環状カーボネートを含有する置換基を2つ有する新規なポリシロキサンおよびその製造方法を提供することにある。

【0004】

【課題を解決するための手段】本発明は、各けい素上に環状カーボネートを含有する置換基を2つ有する新規なポリシロキサンおよびその製造方法を提供する。好ましくは、主鎖が一般式

【0005】

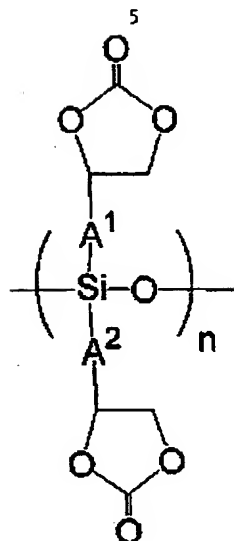
【化8】

40

50

(4)

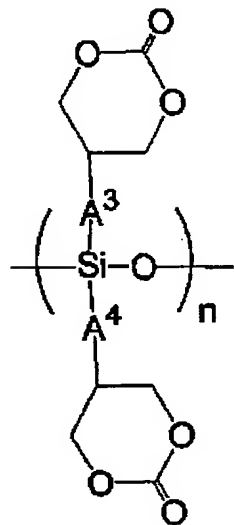
特開平11-302383



【0006】で示される。各ケイ素上に環状エーテルを含有する置換基を2つ有する上記記載のポリシロキサン（式中A'、A'は、置換または非置換のアルキル基、アリール基、またはオキシアルキレン基を、nは1以上の整数を表す）。また好ましくは、主鎖が一般式

【0007】

【化9】



【0008】で示される。各ケイ素上に環状カーボネートを含有する置換基を2つ有する上記記載のポリシロキサン（式中A'、A'は、置換または非置換のアルキル基、アリール基、またはオキシアルキレン基を、nは1以上の整数を表す）。また各ケイ素上に環状カーボネートを含有する置換基を2つ有するシロキサン単位を含むポリシロキサンおよびその製造方法に関する。かかる各ケイ素上に2つの環状カーボネートを含有する置換基を有するポリシロキサンは、少量の他のシロキサン単位、

10

30

40

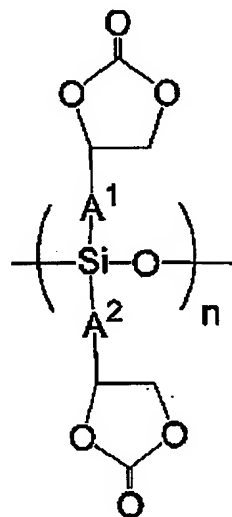
50

6

例えばR<sub>2</sub>SiO<sub>1/2</sub>単位（式中、Rは置換あるいは非置換のアルキル基である）。SiO<sub>1/2</sub>単位を含有しても良い。好ましいものとして、主鎖が一般式

【0009】

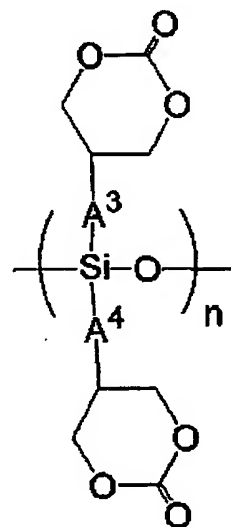
【化10】



【0010】で示される。各ケイ素上に環状カーボネートを含有する置換基を2つ有するシロキサン単位を含有する上記記載のポリシロキサン（式中A'、A'は、置換または非置換のアルキル基、アリール基、またはオキシアルキレン基を、nは1以上の整数を表す）を挙げることができる。また好ましいものとして、主鎖が一般式

【0011】

【化11】



【0012】で示される。各ケイ素上に環状カーボネートを含有する置換基を2つ有するシロキサン単位を含有する上記記載のポリシロキサン（式中A'、A'は、置換

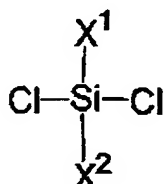
(5)

特開平11-302383

7  
または非置換のアルキル基、アリール基、またはオキシアルキレン基を、 $n$ は1以上の整数を表す)を挙げることができる。上記ポリシロキサン製造法は例えば次に示す方法である。一般式

【0013】

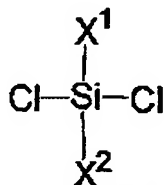
【化12】



【0014】(式中 $X^1$ 、 $X^2$ は環状のカーボネート基を有する置換基であり、 $X^1$ 、 $X^2$ はそれぞれ同種または異種であってもよい)で示されるジクロロシラン誘導体を、プロトン酸を触媒として水の存在下に攪拌することにより、分子鎖両末端にシラノール基を有するジオルガノポリシロキサンを生成せしめ、しかる後に該ジオルガノポリシロキサンを酸性縮合触媒存在下に縮合重合させることを特徴とする、前記各ケイ素上に環状カーボネートを含有する置換基を2つ有する新規なポリシロキサンおよびその製造方法に関する。また本発明は、一般式

【0015】

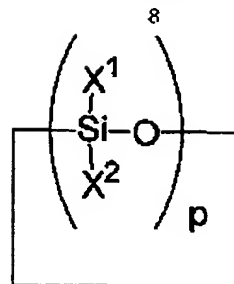
【化13】



【0016】(式中 $X^1$ 、 $X^2$ は環状のカーボネート基を有する置換基であり、 $X^1$ 、 $X^2$ はそれぞれ同種または異種であってもよい)で示されるジクロロシラン誘導体を、酸化亜鉛を有機溶媒の存在下で反応させ、次いで得られた反応混合物に、例えば塩酸などで代表されるプロトン酸を触媒として水の存在下に攪拌することにより、分子鎖両末端にシラノール基を有するジオルガノポリシロキサンを生成せしめ、しかる後に該ジオルガノポリシロキサンを酸性縮合触媒存在下に縮合重合させることを特徴とする、前記各ケイ素上に環状カーボネートを含有する置換基を2つ有する新規なポリシロキサンおよびその製造方法に関する。さらに本発明は、一般式

【0017】

【化14】



10 【0018】(式中 $X^1$ 、 $X^2$ は環状のカーボネート基を有する置換基であり、 $X^1$ 、 $X^2$ はそれぞれ同種または異種であってもよく、 $p$ は3または4)で示されるシクロシロキサン誘導体を、プロトン酸触媒の存在下に重合させることを特徴とする前記各ケイ素上に環状カーボネートを含有する置換基を2つ有する新規なポリシロキサンの製造方法に関する。

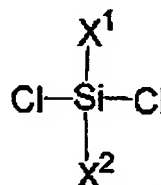
【0019】

【発明の実施の形態】本発明の製造方法を実施するにあたっては、該ジクロロシランに対して酸化亜鉛あるいはプロトン酸を適当な反応容器中で接触させる。本発明においては反応容器の種類は重要でない。しかしながら副反応を防ぐため、非反応性材料で形成された反応容器中でおこなうのが好ましい。本発明方法は、バッチ法、セミバッチ法または連続式で実施しうる。この反応容器は、例えば連続的攪拌タンク反応容器でありうる。この方法はバッチ式あるいは連続式でおこなうのが好ましい。

一般式

【0020】

30 【化15】



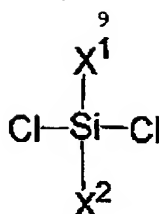
【0021】(式中 $X^1$ 、 $X^2$ は環状のカーボネート基を有する置換基であり、 $X^1$ 、 $X^2$ はそれぞれ同種または異種であってもよい)で示されるジクロロシランに対して酸化亜鉛を有機溶媒の存在下で接触あるいはプロトン酸を接触させるが、その接触方法に特に制約はない。本発明の各ケイ素上に環状カーボネートを含有する置換基を2つ有するポリシロキサンは、一般式

【0022】

【化16】

(6)

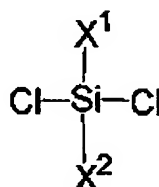
特開平11-302383



【0023】(式中 $\text{X}^1$ 、 $\text{X}^2$ は環状のカーボネート基を有する置換基であり、 $\text{X}^1$ 、 $\text{X}^2$ はそれぞれ同種または異種であってもよい)で表されるジクロロシランと酸化亜鉛を有機溶媒の存在下で反応させ、次いで得られた反応混合物に水およびプロトン酸を加えて攪拌することにより、分子鎖両末端にシラノール基を有するジオルガノポリシロキサンを生成せしめ、次いで該ジオルガノポリシロキサンを酸性縮合触媒の存在下に縮合重合させるのであるが、出発原料である一般式

【0024】

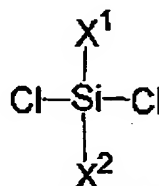
【化17】



【0025】(式中 $\text{X}^1$ 、 $\text{X}^2$ は環状のカーボネート基を有する置換基であり、 $\text{X}^1$ 、 $\text{X}^2$ はそれぞれ同種または異種であってもよい)で示されるジクロロシランは例えば次のような方法で製造される。ジクロロシラン( $\text{H}_2\text{SiCl}_2$ )および環状カーボネート基を含有する末端ビニル化合物を、ヒドロシリル化反応用触媒である白金化合物触媒あるいはロジウム化合物触媒と接触させ付加反応をすることにより得られる。この種のジクロロシランを合成する別の方法としては、例えば、テトラクロロシラン( $\text{SiCl}_4$ )に対して相当するグルニヤール反応剤を反応させて得る方法がある。本発明の各ケイ素上に環状カーボネートを含有する置換基を2つ有するポリシロキサンは前記したような方法で製造された、一般式

【0026】

【化18】



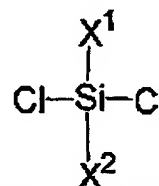
【0027】(式中 $\text{X}^1$ 、 $\text{X}^2$ は環状のカーボネート基を有する置換基であり、 $\text{X}^1$ 、 $\text{X}^2$ はそれぞれ同種または異種であってもよい)で表されるジクロロシランと酸化亜鉛を有機溶媒の存在下で反応させ、次いで、得られた反応混合物に水およびプロトン酸を加えて攪拌することにより、分子末端にシラノール基を有するジオルガノポリ

10

シロキサンを生成せしめるのであるが、ここで酸化亜鉛とジクロロシランは有機溶媒中で反応し、対応するポリシロキサンと副生物として塩化亜鉛を生じる。反応温度は特に限定はされないが、好ましくは $-30^\circ\text{C}$ ~ $200^\circ\text{C}$ の範囲で実施され、さらに好ましくは $50^\circ\text{C}$ ~ $150^\circ\text{C}$ の過熱下で実施される。ここで酸化亜鉛の使用量は、通常、上記ジクロロシラン1モル当たり、0.4~5.0モルとなるような量であり、当量である0.5から4.0モルが好ましい。本発明に使用される有機溶媒は、アセトニトリル、ケトンおよび酢酸アルキルが挙げられる。酢酸アルキルとしては、酢酸メチル、酢酸エチル、酢酸イソプロピル、酢酸*n*-プロピル、酢酸イソブチルなどが例示され、ケトンとしてはメチルエチルケトン、メチルイソブチルケトンが例示されるが、好ましくはアセトニトリル、酢酸メチル、酢酸エチル、酢酸イソブチル、メチルイソブチルケトンが用いられる。またこれらの有機溶媒に、他の有機溶媒を併用することも可能である。引き続いて、水とプロトン酸を加えることにより、分子鎖末端にシラノール基を有するポリシロキサンが生成され、このものは有機溶媒層に溶解し、副生物としての塩化亜鉛は水層に溶解し、また、過剰の酸化亜鉛も水層に溶解して2層に分離される。有機層は純水で洗浄を繰り返した後、回収、脱水される。使用した溶媒は減圧除去等の方法で取り除く。さらに酸性縮合触媒を用いて分子量を増大させることが出来る。酸性縮合触媒としては、濃硫酸、トリフルオロメタンスルホン酸、ドデシルベンゼンスルホン酸などが例示される。また、2-エチルヘキサン酸をテトラメチルグアニジンと当量で混合したものも有効である。室温で縮合反応を起こしシロキサン鎖の切断を起こしにくいので、好ましくはトリフルオロメタンスルホン酸を使用する。縮合反応の温度範囲は特に限定されるものではないが、好ましくは $10^\circ\text{C}$ から $150^\circ\text{C}$ の温度範囲で実施される。また本発明の各ケイ素上に環状カーボネートを含有する置換基を2つ有するポリシロキサンは前記したような方法で製造された、一般式

【0028】

【化19】



【0029】(式中 $\text{X}^1$ 、 $\text{X}^2$ は環状のカーボネート基を有する置換基であり、 $\text{X}^1$ 、 $\text{X}^2$ はそれぞれ同種または異種であってもよい)で表されるジクロロシランと酸を有機溶媒の存在下で反応させ、次いで、得られた反応混合物に水およびプロトン酸を加えて攪拌することにより、分子末端にシラノール基を有するジオルガノポリシロキ



(7)

特開平11-302383

11

12

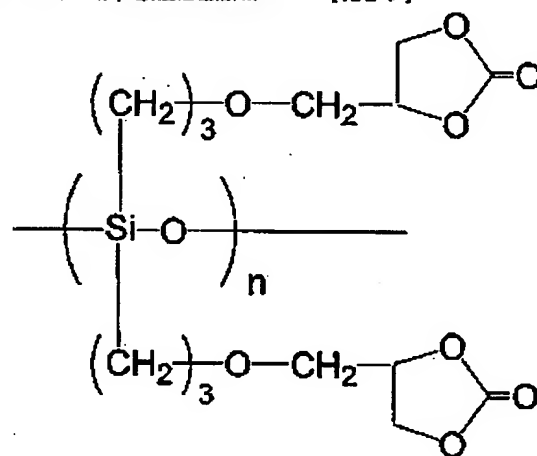
サンを生成せしめるのであるが、ここで使用する酸は特に限定されるものではないが、好ましくは塩酸などが挙げられる。ここで酸の使用量は、通常、上記ジクロシラン1モル当たり、0.4～5.0モルとなるような量であり、当量である0.5から4.0モルが好ましい。本発明に使用される有機溶媒は、ジエチルエーテル、アセトニトリル、ケトンおよび酢酸アルキルが挙げられる。酢酸アルキルとしては、酢酸メチル、酢酸エチル、酢酸イソプロピル、酢酸n-プロピル、酢酸イソブチルなどが例示され、ケトンとしてはメチルエチルケトン、メチルイソブチルケトンなどが例示されるが、好ましくはメチルエチルケトンやメチルイソブチルケトンが用いられる。またこれらの有機溶媒に、他の有機溶媒を併用することも可能である。こうして得られた分子鎖末端にシラノール基を有するポリシロキサンは、酸性縮合触媒\*

\*存在下にさらに重合することが出来る。酸性縮合触媒としては、濃硫酸、トリフルオロメタンスルホン酸、ドデシルベンゼンスルホン酸などが例示される。また、2-エチルヘキサン酸をテトラメチルグアニジンと当量で混合したものも有効である。室温で縮合反応を起こしシロキサン鎖の切断を起こしにくいので、好ましくはトリフルオロメタンスルホン酸を使用する。縮合反応の温度範囲は特に限定されるものではないが、好ましくは室温から150℃の温度範囲で実施される。このような方法により得られる該ポリシロキサンの化合物例を示すが、本発明は以下の化合物に限定されるものではない。なお化合物1～6において、nは1以上の整数を表す。

(化合物例1)

【0030】

【化20】

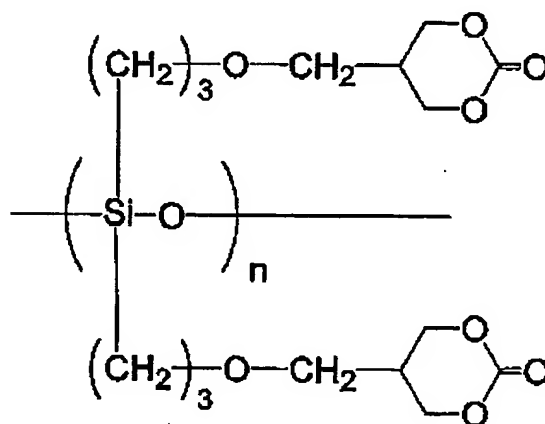


【0031】(化合物例2)

【0032】

※【化21】

※



【0033】(化合物例3)

【0034】

【化22】

(9)

特開平11-302383

15

16

い。

(実施例1) ガラス内筒を備えたステンレス製オートクレーブに、環状(3-ブテニル)エチレンエステルカルボン酸14.2gおよび白金ビニルシロキサンキシレン溶液1.0mg ( $1.0 \times 10^{-4}$  mmol)を秤取し、空气中でそのオートクレーブに、ジクロロシラン2.15gを加え、60℃に加熱して攪拌した。6時間後反応を終了し反応混合物をクーゲルロールを使用して蒸留した。その結果ケイ素上に環状カーボネート基を2つ有するジクロロシラン誘導体が、5.65g (14.7 mmol, 収率88%)得られた。またこの物質のGC-MSによる分子量測定では親ピークが385に現れた。次に得られたジクロロシラン誘導体3.84gを、酸化亜鉛1.22g、酢酸エチル5.0gの入った反応容器に、60℃に加熱攪拌下で1時間かけて滴下した。その

後さらに3時間加熱攪拌を行なった。冷却後純水20gを加え、さらに10%塩酸水をフラスコの固形分がなくなるまで添加した。有機層を取り出し純水で十分洗浄したのち、有機溶媒を減圧除去することによりポリシロキサン3.15gを得た。このポリシロキサン0.8gと過塩素酸リチウム0.2gとをアセトンに溶解させ均一溶液とし、それを基板上に流延した後、アルゴンガス雰囲気下で加熱して溶媒を除去し薄膜を得た。この薄膜のイオン伝導度は極めて高い値を示した。

【0042】

【発明の効果】本発明の各ケイ素上に環状カーボネートを含有する置換基を2つ有するポリシロキサンは新規な化合物であり、またその製造方法は簡便で効率が良いという特徴を有する。

## \*NOTICES\*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

 CLAIMS
 

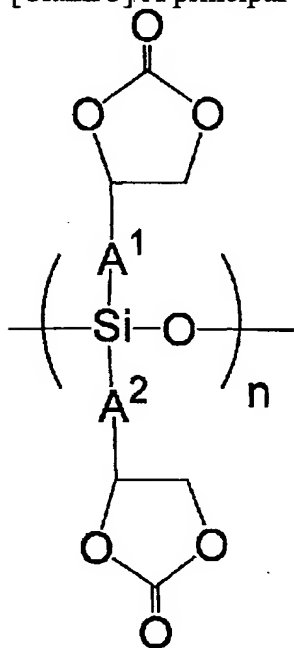
---

[Claim(s)]

[Claim 1] The polysiloxane which has two substituents which contain annular carbonate on each silicon.

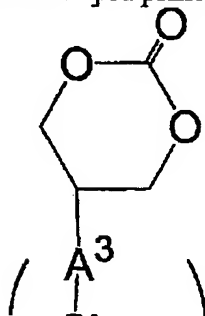
[Claim 2] A polysiloxane including the siloxane unit which has two substituents which contain annular carbonate on each silicon.

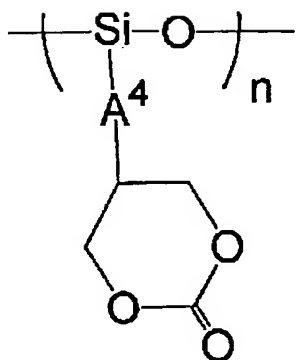
[Claim 3] A principal chain is a general formula. [Formula 1]



The polysiloxane according to claim 1, which comes out and has two substituents which are shown, and which contain annular carbonate on each silicon. (As for the inside A<sup>1</sup> and A<sup>2</sup> of a formula, n expresses one or more integers for substitution or an unsubstituted alkyl group, an aryl group, or an oxy-alkylene machine)

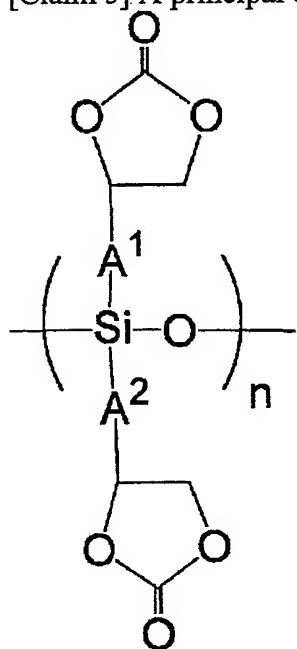
[Claim 4] A principal chain is a general formula. [Formula 2]





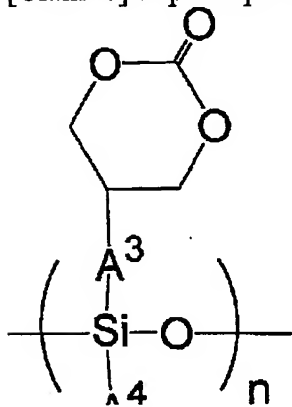
The polysiloxane according to claim 1 which comes out and has two substituents which are shown, and which contain annular carbonate on each silicon. (As for the inside A3 and A4 of a formula, n expresses one or more integers for substitution or an unsubstituted alkyl group, an aryl group, or an oxy-alkylene machine)

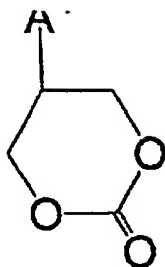
[Claim 5] A principal chain is a general formula. [Formula 3]



The polysiloxane according to claim 2 which comes out and contains the siloxane unit which is shown, and which has two substituents which contain annular carbonate on each silicon. (As for the inside A1 and A2 of a formula, n expresses one or more integers for substitution or an unsubstituted alkyl group, an aryl group, or an oxy-alkylene machine)

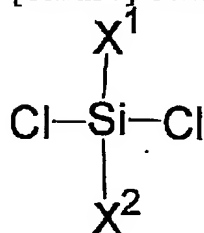
[Claim 6] A principal chain is a general formula. [Formula 4]



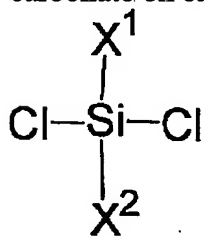


The polysiloxane according to claim 2 which comes out and contains the siloxane unit which is shown, and which has two substituents which contain annular carbonate on each silicon. (As for the inside A3 and A4 of a formula, n expresses one or more integers for substitution or an unsubstituted alkyl group, an aryl group, or an oxy-alkylene machine)

[Claim 7] General formula. [Formula 5]

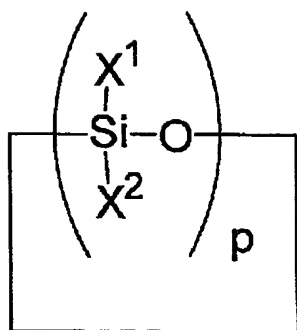


JIO characterized by providing the following. It is the dichlorosilane derivative shown by (the inside X1 and X2 of a formula being the substituent which has an annular carbonate machine, and being that X1 and X2 are of the same kind respectively or different species). The manufacture method of a polysiloxane which chain both ends are made to generate a silanol-group luganot polysiloxane, and is characterized by making after an appropriate time carry out the condensation polymerization of this diorganopolysiloxane to the bottom of existence of an acid condensation catalyst by making a zinc oxide react under existence of an organic solvent, and subsequently adding and stirring water and a proton acid into the obtained reaction mixture of having two substituents which contain annular carbonate on each silicon according to claim 1. [Claim 8] General formula. [Formula 6]



The dichlorosilane derivative shown by (the inside X1 and X2 of a formula being the substituent which has an annular carbonate machine, and being that X1 and X2 are of the same kind respectively or different species) Chain both ends are made to generate the diorganopolysiloxane which has a silanol group by mixing under existence of a solvent by making an acid into a catalyst. The manufacture method of a polysiloxane characterized by making after an appropriate time carry out the condensation polymerization of this diorganopolysiloxane to the bottom of existence of an acid condensation catalyst of having two annular carbonate machines as a substituent on each silicon according to claim 1.

[Claim 9] General formula. [Formula 7]



(-- the substituent which has a carbonate machine annular the inside X1 and X2 of a formula -- it is -- that X1 and X2 are of the same kind respectively or the manufacture method of a polysiloxane which may be different species and is characterized by p carrying out the polymerization of the cyclosiloxane derivative shown by 3 or 4) to the bottom of existence of a proton-acid catalyst of having two annular carbonate machines as a substituent on each silicon according to claim 1.

---

[Translation done.]

## \* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---



---

DETAILED DESCRIPTION

---



---

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the polysiloxane which has two substituents which contain annular carbonate on a cell etc. on each silicon which may become an usable solid polymer electrolyte etc., and its manufacture method.

[0002]

[Description of the Prior Art] While resin industry develops in recent years, the resin which has a special property is needed and development of the macromolecule which is not in the former in connection with it has come to be desired. The uses of the polyether obtained by the ring opening polymerization of an epoxy compound, such as special rubber and a surfactant, are large. Moreover, the macromolecule which has a polyethylene oxide in a side chain can solubilize alkali-metal salts, such as lithium salt, and the research to a polyelectrolyte is prosperous in it. However, a polyethylene oxide cannot fully raise mobility of a metal salt for [ the ] high crystallinity.

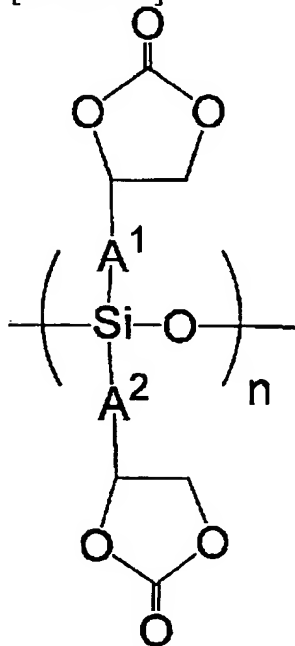
[0003]

[Problem(s) to be Solved by the Invention] this invention is to offer the new polysiloxane which has two substituents which contain annular carbonate on each silicon, and its manufacture method.

[0004]

[Means for Solving the Problem] this invention offers the new polysiloxane which has two substituents which contain annular carbonate on each silicon, and its manufacture method. Preferably, a principal chain is a general formula. [0005]

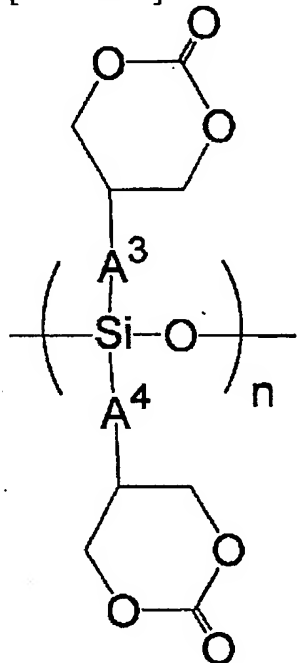
[Formula 8]



[0006] The polysiloxane of the above-mentioned publication which comes out and has two substituents which are shown, and which contain cyclic ether on each silicon (as for the inside A1 and A2 of a formula, n expresses one or more integers for substitution or an unsubstituted alkyl group, an aryl group, or an oxy-alkylene machine). Moreover, a principal chain is a general formula preferably.

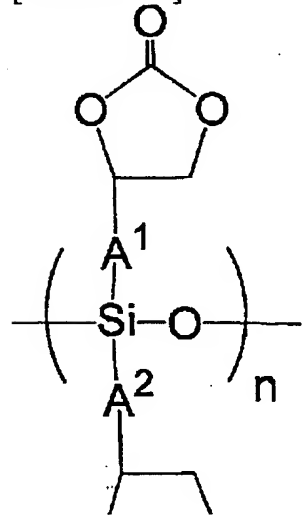
[0007]

[Formula 9]

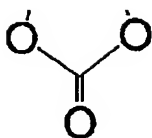


[0008] The polysiloxane of the above-mentioned publication which comes out and has two substituents which are shown, and which contain annular carbonate on each silicon (as for the inside A3 and A4 of a formula, n expresses one or more integers for substitution or an unsubstituted alkyl group, an aryl group, or an oxy-alkylene machine). Moreover, it is related with a polysiloxane including the siloxane unit which has two substituents which contain annular carbonate on each silicon, and its manufacture method. The polysiloxane which has the substituent which contains two annular carbonate on each of this silicon may contain other little siloxane units (the inside of a formula and R are substitution or an unsubstituted alkyl group), for example, R<sub>3</sub>SiO<sub>3/2</sub> unit, and SiO<sub>4/2</sub> unit. As a desirable thing, a principal chain is a general formula. [0009]

[Formula 10]

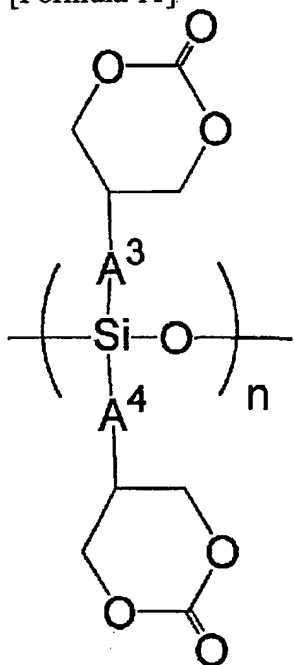






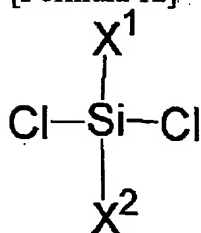
[0010] It can come out and the polysiloxane (as for the inside A1 and A2 of a formula, n expresses one or more integers for substitution or an unsubstituted alkyl group, an aryl group, or an oxy-alkylene machine) of the above-mentioned publication containing the siloxane unit which has two substituents which contain annular carbonate on each silicon shown can be mentioned. Moreover, as a desirable thing, a principal chain is a general formula. [0011]

[Formula 11]



[0012] It can come out and the polysiloxane (as for the inside A3 and A4 of a formula, n expresses one or more integers for substitution or an unsubstituted alkyl group, an aryl group, or an oxy-alkylene machine) of the above-mentioned publication containing the siloxane unit which has two substituents which contain annular carbonate on each silicon shown can be mentioned. The manufacturing method of the above-mentioned polysiloxane is a method shown below. General formula. [0013]

[Formula 12].

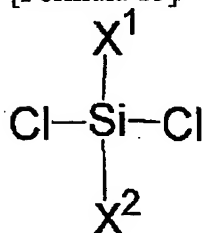


[0014] By stirring the dichlorosilane derivative shown by (the inside X1 and X2 of a formula being the substituent which has an annular carbonate machine, and being that X1 and X2 are of the same kind respectively or different species) under existence of water by making a proton acid into a catalyst Chain both ends are made to generate the diorganopolysiloxane which has a silanol group. It is related with the new polysiloxane which is characterized by making after an appropriate time carry out the condensation polymerization of this diorganopolysiloxane to the bottom of acid condensation

catalyst existence and which has two substituents which contain annular carbonate on each aforementioned silicon, and its manufacture method. Moreover, this invention is a general formula.

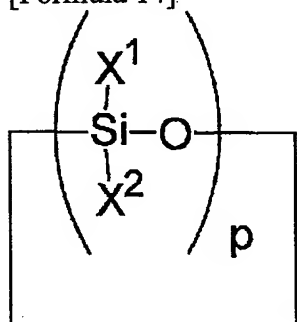
[0015]

[Formula 13]



[0016] The dichlorosilane derivative shown by (the inside X1 and X2 of a formula being the substituent which has an annular carbonate machine, and being that X1 and X2 are of the same kind respectively or different species) Into the reaction mixture which the zinc oxide was made to react under existence of an organic solvent, and was subsequently obtained, for example, by stirring under existence of water by making into a catalyst the proton acid represented with a hydrochloric acid etc. Chain both ends are made to generate the diorganopolysiloxane which has a silanol group. It is related with the new polysiloxane which is characterized by making after an appropriate time carry out the condensation polymerization of this diorganopolysiloxane to the bottom of acid condensation catalyst existence and which has two substituents which contain an annular carbonate machine on each aforementioned silicon, and its manufacture method. Furthermore, this invention is a general formula. [0017]

[Formula 14]



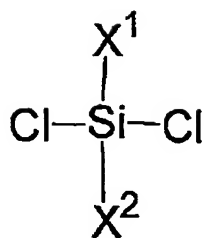
[0018] (-- the inside X1 and X2 of a formula is the substituent which has an annular carbonate machine, and is related with the manufacture method of that X1 and X2 are of the same kind respectively or the new polysiloxane which has two substituents which contain annular carbonate on each aforementioned silicon which may be different species and is characterized by p carrying out the polymerization of the cyclosiloxane derivative shown by 3 or 4) to the bottom of existence of a proton-acid catalyst

[0019]

[Embodiments of the Invention] If it hits enforcing the manufacture method of this invention, a zinc oxide or a proton acid is contacted in a suitable reaction container to this dichlorosilane. In this invention, the kind of reaction container is not important. However, in order to prevent side reaction, it is desirable to carry out in the reaction container formed with non-reactivity material. this invention method can be enforced with a batch method, a semi batch method, or continuous system. This reaction container is for example, a continuous stirring tank reaction container, and it deals in it. As for this method, it is desirable that a batch type or continuous system performs.

General formula. [0020]

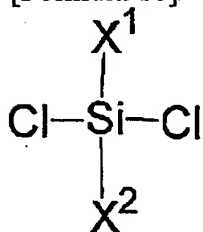
[Formula 15]



[0021] Although a zinc oxide contacts contact or a proton acid under existence of an organic solvent to the dichlorosilane shown by (the inside X1 and X2 of a formula being the substituent which has an annular carbonate machine, and being that X1 and X2 are of the same kind respectively or different species), there are especially no restrictions in the contact method. The polysiloxane which has two substituents which contain annular carbonate on each silicon of this invention is a general formula.

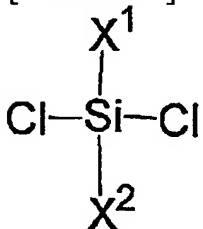
[0022]

[Formula 16]



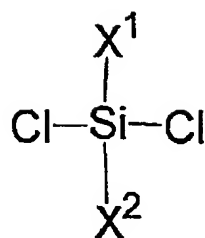
[0023] The dichlorosilane and the zinc oxide which are expressed with (the inside X1 and X2 of a formula being the substituent which has an annular carbonate machine, and being that X1 and X2 are of the same kind respectively or different species) are made to react under existence of an organic solvent. Subsequently, although chain both ends are made to generate the diorganopolysiloxane which has a silanol group and the condensation polymerization of this diorganopolysiloxane is carried out subsequently to the bottom of existence of an acid condensation catalyst by adding and stirring water and a proton acid into the obtained reaction mixture. The general formula which is a first train raw material. [0024]

[Formula 17]



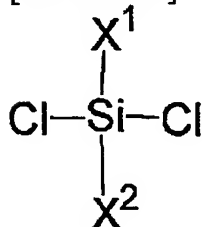
[0025] The dichlorosilane shown by (the inside X1 and X2 of a formula being the substituent which has an annular carbonate machine, and being that X1 and X2 are of the same kind respectively or different species) is manufactured, for example by the following methods. It is obtained by contacting the end vinyl compound containing dichlorosilane ( $\text{H}_2\text{SiCl}_2$ ) and an annular carbonate machine for the platinum compound catalyst or rhodium compound catalyst which is a catalyst for a hydrosilylation reaction, and carrying out an addition reaction. As an option which compounds this kind of dichlorosilane, there is the method of making the GURUNI yard reaction agent which corresponds to a tetrapod chlorosilicane ( $\text{SiCl}_4$ ) react, and acquiring, for example. The polysiloxane which has two substituents which contain annular carbonate on each silicon of this invention is the general formula manufactured by method which was described above. [0026]

[Formula 18]



[0027] The dichlorosilane and the zinc oxide which are expressed with (the inside X1 and X2 of a formula being the substituent which has an annular carbonate machine, and being that X1 and X2 are of the same kind respectively or different species) are made to react under existence of an organic solvent. subsequently Although a molecule end is made to generate the diorganopolysiloxane which has a silanol group by added and stirring water and a proton acid into the obtained reaction mixture A zinc oxide and dichlorosilane react in an organic solvent, and produce a zinc chloride as a corresponding polysiloxane and a corresponding by-product here. Although especially limitation is not carried out, reaction temperature is preferably carried out in -30 degrees C - 200 degrees C, and is carried out under 50 degrees C - 150 degrees C overheating still more preferably. The amount of the zinc oxide used usually has desirable 0.5 to 4.0 which is the amount which becomes 0.4-5.0 mols per one mol of above-mentioned dichlorosilane, and is the equivalent mols here. As for the organic solvent used for this invention, an acetonitrile, a ketone, and an acetic-acid alkyl are mentioned. Although methyl acetate, ethyl acetate, an isopropyl acetate, n propyl acetate, an isobutyl acetate, etc. are illustrated and a methyl ethyl ketone and a methyl isobutyl ketone are illustrated as a ketone as an acetic-acid alkyl, an acetonitrile, methyl acetate, ethyl acetate, an isobutyl acetate, and a methyl isobutyl ketone are used preferably. Moreover, it is also possible to use other organic solvents together to these organic solvents. Then, by adding water and a proton acid, the polysiloxane which has a silanol group at the chain end is generated, this thing is dissolved in an organic-solvent layer, and the zinc chloride as a by-product dissolves in a water layer, and a superfluous zinc oxide also dissolves in a water layer, and it separates into two-layer. After an organic layer repeats washing with pure water, it is collected and dehydrated. The used solvent is removed by methods, such as reduced pressure removal. Furthermore, molecular weight can be increased using an acid condensation catalyst. As an acid condensation catalyst, a concentrated sulfuric acid, a trifluoromethane sulfonic acid, dodecylbenzenesulfonic acid, etc. are illustrated. Moreover, what mixed 2-ethyl hexanoic acid with tetramethyl guanidine by this mol is effective. Since a condensation reaction is started at a room temperature and it is hard to start a siloxane chain scission, a trifluoromethane sulfonic acid is used preferably. Although especially the temperature requirement of a condensation reaction is not limited, it is preferably carried out by the 10 to 150 degrees C temperature requirement. Moreover, the polysiloxane which has two substituents which contain annular carbonate on each silicon of this invention is the general formula manufactured by method which was described above. [0028]

[Formula 19]



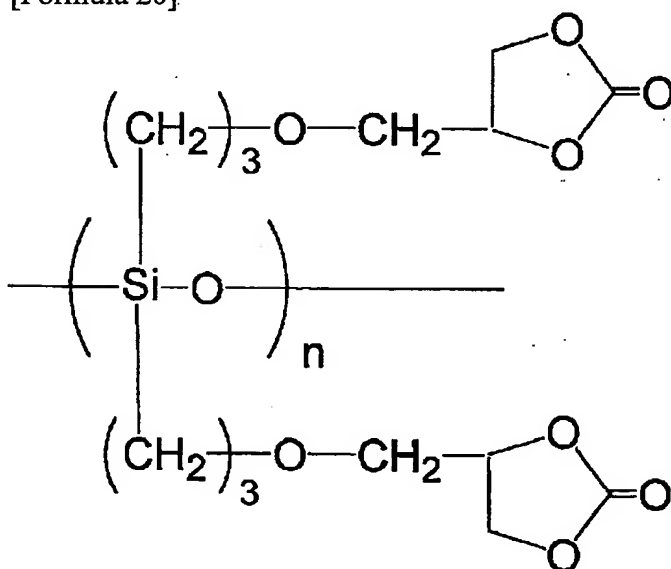
[0029] The dichlorosilane and the acid which are expressed with (the inside X1 and X2 of a formula being the substituent which has an annular carbonate machine, and being that X1 and X2 are of the same kind respectively or different species) are made to react under existence of an organic solvent. subsequently Although especially the acid used here although a molecule end is made to generate the

diorganopolysiloxane which has a silanol group by added and stirring water and a proton acid into the obtained reaction mixture is not limited, a hydrochloric acid etc. is mentioned preferably. The amount of the acid used usually has desirable 0.5 to 4.0 which is the amount which becomes 0.4-5.0 mols per one mol of above-mentioned dichlorosilane, and is the equivalent mols here. As for the organic solvent used for this invention, diethylether, an acetonitrile, a ketone, and an acetic-acid alkyl are mentioned. Although methyl acetate, ethyl acetate, an isopropyl acetate, n propyl acetate, an isobutyl acetate, etc. are illustrated and a methyl ethyl ketone, a methyl isobutyl ketone, etc. are illustrated as a ketone as an acetic-acid alkyl, a methyl ethyl ketone and a methyl isobutyl ketone are used preferably. Moreover, it is also possible to use other organic solvents together to these organic solvents. In this way, the polymerization of the polysiloxane which has a silanol group at the obtained chain end can be further carried out to the bottom of acid condensation catalyst existence. As an acid condensation catalyst, a concentrated sulfuric acid, a trifluoromethane sulfonic acid, dodecylbenzenesulfonic acid, etc. are illustrated. Moreover, what mixed 2-ethyl hexanoic acid with tetramethyl guanidine by this mol is effective. Since a condensation reaction is started at a room temperature and it is hard to start a siloxane chain scission, a trifluoromethane sulfonic acid is used preferably. Although especially the temperature requirement of a condensation reaction is not limited, it is preferably carried out by the 150-degree C temperature requirement from a room temperature. Although the example of a compound of this polysiloxane obtained by such method is shown, this invention is not limited to the following compounds. In addition, in compounds 1-6, n expresses one or more integers.

(Example 1 of a compound)

[0030]

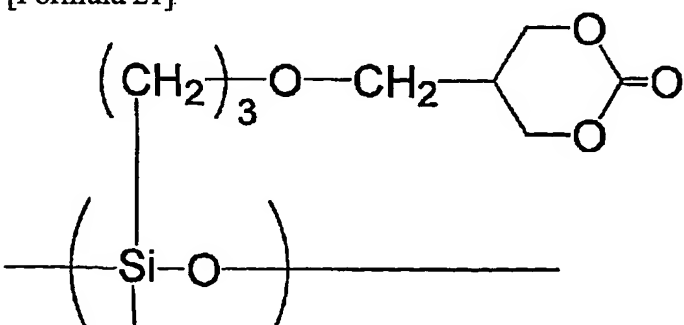
[Formula 20]

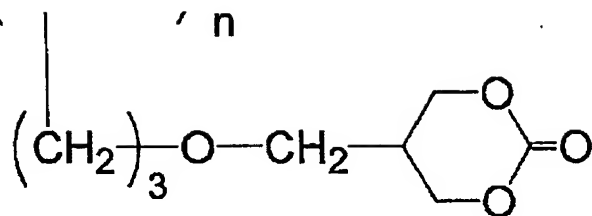


[0031] (Example 2 of a compound)

[0032]

[Formula 21]

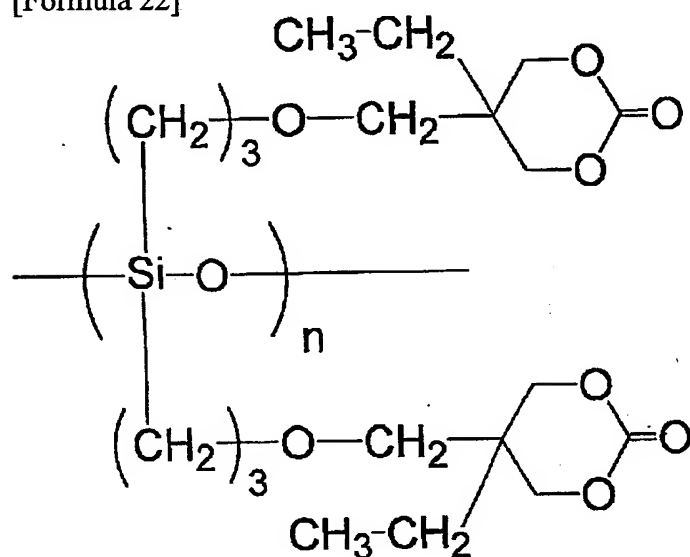




[0033] (Example 3. of a compound).

[0034]

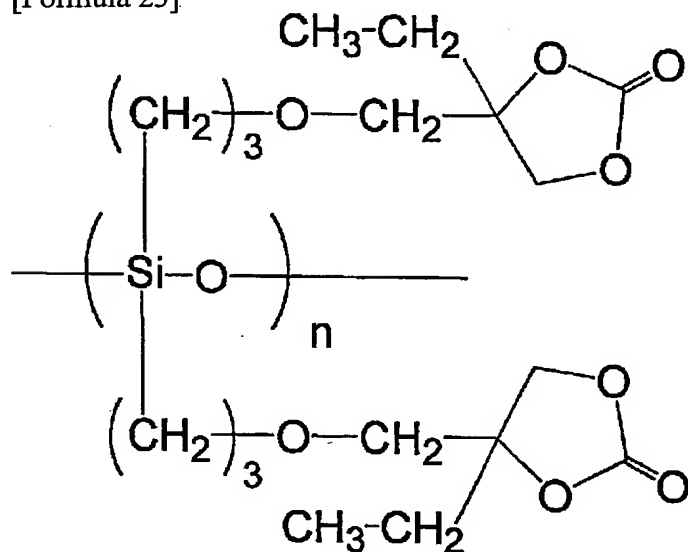
[Formula 22]



[0035] (Example 4. of a compound)

[0036].

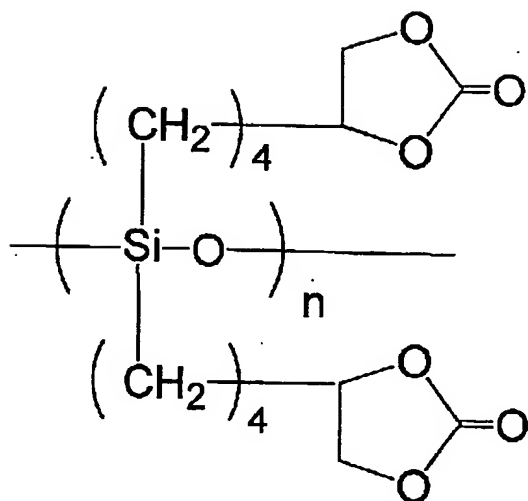
[Formula 23].



[0037] (Example 5. of a compound).

[0038].

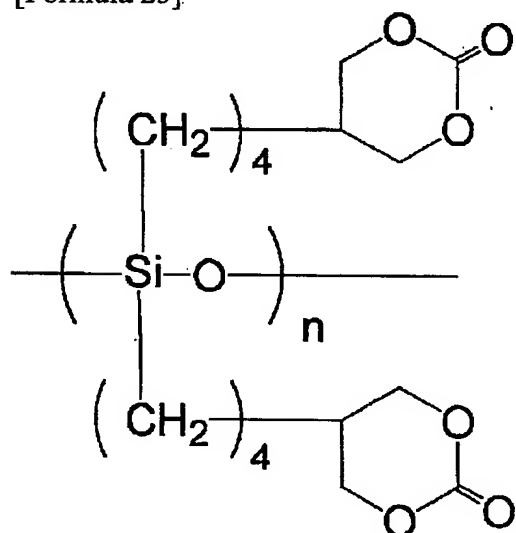
[Formula 24].



[0039] (Example 6 of a compound)

[0040]

[Formula 25]



[0041]

[Example] Next, although the example of this invention is explained concretely, this invention is not limited to the following examples.

(Example 1) To the autoclave made from stainless steel equipped with the glass container liner, 14.2g of annular (3-butenyl) ethylene ester carboxylic acids and 1.0mg (1.0x10<sup>-4</sup>mmol) of platinum vinyl siloxane xylene solutions were \*\*\*\*(ed), and in air, dichlorosilane 2.15g was added, and it heated and stirred at 60 degrees C at the autoclave. The reaction 6 hours after was ended and reaction mixture was distilled using the KUGERU roll. 5.65g (14.7mmol, 88% of yield) of dichlorosilane derivatives which, as a result, have two annular carbonate machines on silicon was obtained. Moreover, in the determination of molecular weight by GC-MS of this matter, the parent peak appeared in 385. Next, it was dropped at 1.22g of zinc oxides, and the reaction container of 5.0g of ethyl acetate into which it went, having dichlorosilane covered [ which was obtained / 3.84g ] it over 60 degrees C under heating.stirring for 1 hour. Heating stirring was performed after that for further 3 hours. 20g of pure water after cooling was added, and it added until the solid content of a flask was lost in hydrochloric-acid water 10 more%. After it took out the organic layer and pure water washed enough, polysiloxane 3.15g was obtained by carrying out reduced pressure removal of the organic solvent. After having dissolved these polysiloxane 0.8g and 0.2g of lithium perchlorates in the

acetone, considering as the uniform solution and casting it on a substrate, it heated under argon gas atmosphere, the solvent was removed, and the thin film was obtained. The ionic conductivity of this thin film showed the very high value.

[0042]

[Effect of the Invention] The polysiloxane which has two substituents which contain annular carbonate on each silicon of this invention is a new compound, and it has the feature that the manufacture method is simple and it is efficient.

---

[Translation done.]



\* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation..

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

TECHNICAL FIELD

---

[The technical field to which invention belongs] this invention relates to the polysiloxane which has two substituents which contain annular carbonate on a cell etc. on each silicon which may become an usable solid polymer electrolyte etc., and its manufacture method.

---

[Translation done.]

\* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation..

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

PRIOR ART

---

[Description of the Prior Art] While resin industry develops in recent years, the resin which has a special property is needed and development of the macromolecule which is not in the former in connection with it has come to be desired. The uses of the polyether obtained by the ring opening polymerization of an epoxy compound, such as special rubber and a surfactant, are large. Moreover, the macromolecule which has a polyethylene oxide in a side chain can solubilize alkali-metal salts, such as lithium salt, and the research to a polyelectrolyte is prosperous in it. However, a polyethylene oxide cannot fully raise mobility of a metal salt for [ the ] high crystallinity.

---

[Translation done.]

\* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

EFFECT OF THE INVENTION

---

[Effect of the Invention] The polysiloxane which has two substituents which contain annular carbonate on each silicon of this invention is a new compound, and it has the feature that the manufacture method is simple and it is efficient.

---

[Translation done.]

---

\*NOTICES\*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

TECHNICAL PROBLEM

---

[Problem(s) to be Solved by the Invention] this invention is to offer the new polysiloxane which has two substituents which contain annular carbonate on each silicon, and its manufacture method.

---

[Translation done.]

## \* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

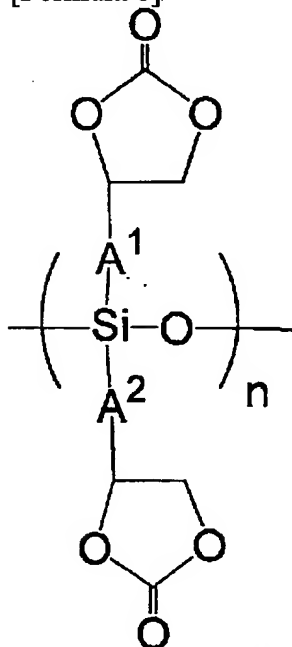
---

MEANS

---

[Means for Solving the Problem] this invention offers the new polysiloxane which has two substituents which contain annular carbonate on each silicon, and its manufacture method. Preferably, a principal chain is a general formula. [0005]

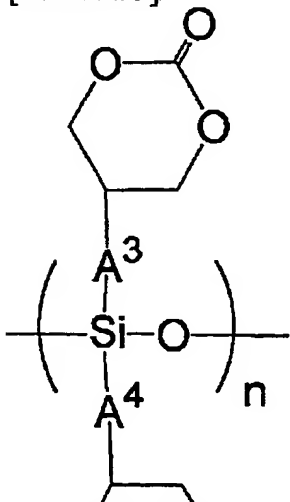
[Formula 8]

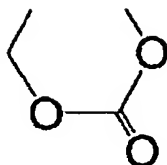


[0006] The polysiloxane of the above-mentioned publication which comes out and has two substituents which are shown, and which contain cyclic ether on each silicon (as for the inside A1. and A2 of a formula, n expresses one or more integers for substitution or an unsubstituted alkyl group, an aryl group, or an oxy-alkylene machine). Moreover, a principal chain is a general formula preferably.

[0007]

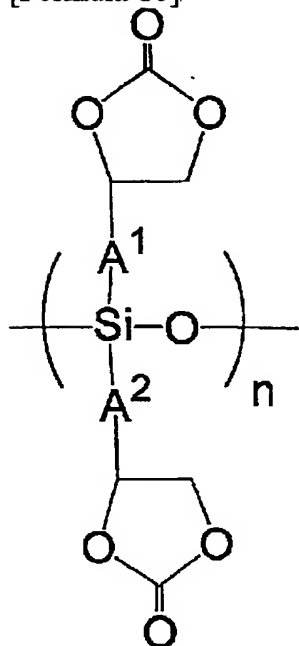
[Formula 9]





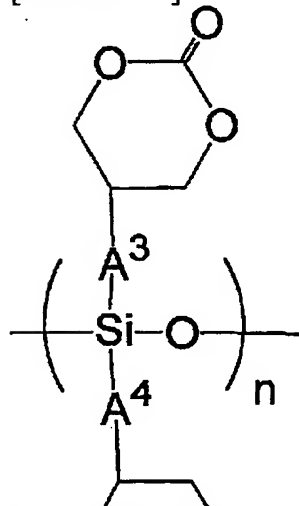
[0008] The polysiloxane of the above-mentioned publication which comes out and has two substituents which are shown, and which contain annular carbonate on each silicon (as for the inside A3 and A4 of a formula, n expresses one or more integers for substitution or an unsubstituted alkyl group, an aryl group, or an oxy-alkylene machine). Moreover, it is related with a polysiloxane including the siloxane unit which has two substituents which contain annular carbonate on each silicon, and its manufacture method. The polysiloxane which has the substituent which contains two annular carbonate on each of this silicon may contain other little siloxane units (the inside of a formula and R are substitution or an unsubstituted alkyl group), for example,  $R_3SiO_{3/2}$  unit, and  $SiO_{4/2}$  unit. As a desirable thing, a principal chain is a general formula. [0009]

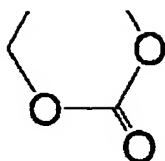
[Formula 10]



[0010] It can come out and the polysiloxane (as for the inside A1 and A2 of a formula, n expresses one or more integers for substitution or an unsubstituted alkyl group, an aryl group, or an oxy-alkylene machine) of the above-mentioned publication containing the siloxane unit which has two substituents which contain annular carbonate on each silicon shown can be mentioned. Moreover, as a desirable thing, a principal chain is a general formula. [0011]

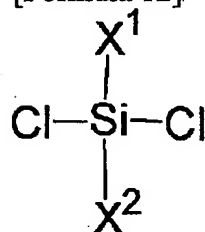
[Formula 11]





[0012] It can come out and the polysiloxane (as for the inside A3 and A4 of a formula, n expresses one or more integers for substitution or an unsubstituted alkyl group, an aryl group, or an oxy-alkylene machine) of the above-mentioned publication containing the siloxane unit which has two substituents which contain annular carbonate on each silicon shown can be mentioned. The manufacturing method of the above-mentioned polysiloxane is a method shown below. General formula. [0013]

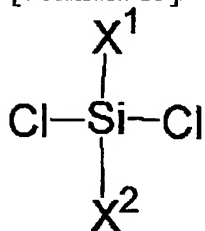
[Formula 12]



[0014] By stirring the dichlorosilane derivative shown by (the inside X1 and X2 of a formula being the substituent which has an annular carbonate machine, and being that X1 and X2 are of the same kind respectively or different species) under existence of water by making a proton acid into a catalyst Chain both ends are made to generate the diorganopolysiloxane which has a silanol group. It is related with the new polysiloxane which is characterized by making after an appropriate time carry out the condensation polymerization of this diorganopolysiloxane to the bottom of acid condensation catalyst existence and which has two substituents which contain annular carbonate on each aforementioned silicon, and its manufacture method. Moreover, this invention is a general formula.

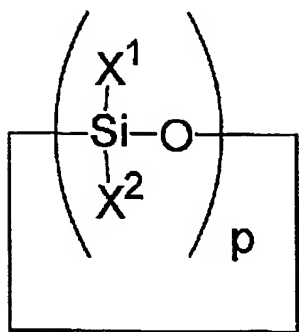
[0015]

[Formula 13]



[0016] The dichlorosilane derivative shown by (the inside X1 and X2 of a formula being the substituent which has an annular carbonate machine, and being that X1 and X2 are of the same kind respectively or different species) Into the reaction mixture which the zinc oxide was made to react under existence of an organic solvent, and was subsequently obtained, for example, by stirring under existence of water by making into a catalyst the proton acid represented with a hydrochloric acid etc. Chain both ends are made to generate the diorganopolysiloxane which has a silanol group. It is related with the new polysiloxane which is characterized by making after an appropriate time carry out the condensation polymerization of this diorganopolysiloxane to the bottom of acid condensation catalyst existence and which has two substituents which contain an annular carbonate machine on each aforementioned silicon, and its manufacture method. Furthermore, this invention is a general formula. [0017]

[Formula 14]



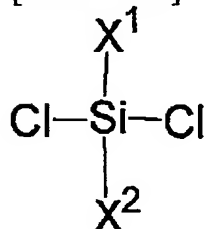
[0018] (-- the inside X1 and X2 of a formula is the substituent which has an annular carbonate machine, X1 and X2 may be a homotypic or different species, respectively, and p is related with the manufacture method of a new polysiloxane of having two substituents which contain annular carbonate on each aforementioned silicon characterized by carrying out the polymerization of the cyclosiloxane derivative shown by 3 or 4) to the bottom of existence of a proton-acid catalyst

[0019]

[Embodiments of the Invention] If it hits enforcing the manufacture method of this invention, a zinc oxide or a proton acid is contacted in a suitable reaction container to this dichlorosilane. In this invention, the kind of reaction container is not important. However, in order to prevent side reaction, it is desirable to carry out in the reaction container formed with non-reactivity material. this invention method can be enforced with a batch method, a semi batch method, or continuous system. This reaction container is for example, a continuous stirring tank reaction container, and it deals in it. As for this method, it is desirable that a batch type or continuous system performs.

General formula. [0020]

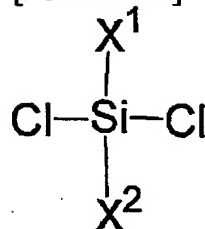
[Formula 15]



[0021] Although a zinc oxide contacts contact or a proton acid under existence of an organic solvent to the dichlorosilane shown by (the inside X1 and X2 of a formula may be the substituent which has an annular carbonate machine, and X1 and X2 may be a homotypic or different species, respectively), there are especially no restrictions in the contact method. The polysiloxane which has two substituents which contain annular carbonate on each silicon of this invention is a general formula.

[0022]

[Formula 16]

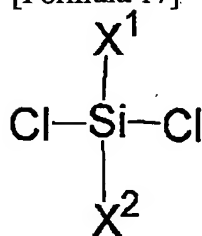


[0023] The dichlorosilane and the zinc oxide which are expressed with (the inside X1 and X2 of a formula may be the substituent which has an annular carbonate machine, and X1 and X2 may be a homotypic or different species, respectively) are made to react under existence of an organic solvent. Subsequently, although chain both ends are made to generate the diorganopolysiloxane which has a silanol group and the condensation polymerization of this diorganopolysiloxane is carried out subsequently to the bottom of existence of an acid condensation catalyst by adding and stirring water and a proton acid into the obtained reaction mixture The general formula which is a first train raw



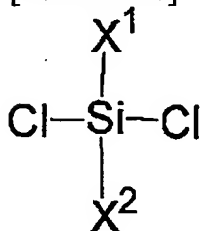
material. [0024]

[Formula 17]



[0025] The dichlorosilane shown by (the inside X1 and X2 of a formula may be the substituent which has an annular carbonate machine, and X1 and X2 may be a homotypic or different species, respectively) is manufactured, for example by the following methods. It is obtained by contacting the end vinyl compound containing dichlorosilane ( $H_2SiCl_2$ ) and an annular carbonate machine for the platinum compound catalyst or rhodium compound catalyst which is a catalyst for a hydrosilylation reaction, and carrying out an addition reaction. As an option which compounds this kind of dichlorosilane, there is the method of making the GURUNI yard reaction agent which corresponds to a tetrapod chlorosilicane ( $SiCl_4$ ) react, and acquiring, for example. The polysiloxane which has two substituents which contain annular carbonate on each silicon of this invention is the general formula manufactured by method which was described above. [0026]

[Formula 18]

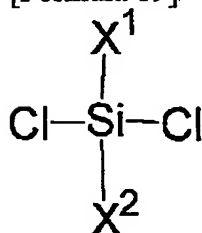


[0027] The dichlorosilane and the zinc oxide which are expressed with (the inside X1 and X2 of a formula may be the substituent which has an annular carbonate machine, and X1 and X2 may be a homotypic or different species, respectively) are made to react under existence of an organic solvent. subsequently Although a molecule end is made to generate the diorganopolysiloxane which has a silanol group by added and stirring water and a proton acid into the obtained reaction mixture. A zinc oxide and dichlorosilane react in an organic solvent, and produce a zinc chloride as a corresponding polysiloxane and a corresponding by-product here. Although especially limitation is not carried out, reaction temperature is preferably carried out in -30 degrees C - 200 degrees C, and is carried out under 50 degrees C - 150 degrees C overheating still more preferably. The amount of the zinc oxide used usually has desirable 0.5 to 4.0 which is the amount which becomes 0.4-5.0 mols per one mol of above-mentioned dichlorosilane, and is the equivalent mols here. As for the organic solvent used for this invention, an acetonitrile, a ketone, and an acetic-acid alkyl are mentioned. Although methyl acetate, ethyl acetate, an isopropyl acetate, n propyl acetate, an isobutyl acetate, etc. are illustrated and a methyl ethyl ketone and a methyl isobutyl ketone are illustrated as a ketone as an acetic-acid alkyl, an acetonitrile, methyl acetate, ethyl acetate, an isobutyl acetate, and a methyl isobutyl ketone are used preferably. Moreover, it is also possible to use other organic solvents together to these organic solvents. Then, by adding water and a proton acid, the polysiloxane which has a silanol group at the chain end is generated, this thing is dissolved in an organic-solvent layer, and the zinc chloride as a by-product dissolves in a water layer, and a superfluous zinc oxide also dissolves in a water layer, and it separates into two-layer. After an organic layer repeats washing with pure water, it is collected and dehydrated. The used solvent is removed by methods, such as reduced pressure removal.

Furthermore, molecular weight can be increased using an acid condensation catalyst. As an acid condensation catalyst, a concentrated sulfuric acid, a trifluoromethane sulfonic acid, dodecylbenzenesulfonic acid, etc. are illustrated. Moreover, what mixed 2-ethyl hexanoic acid with tetramethyl guanidine by this mol is effective. Since a condensation reaction is started at a room temperature and it is hard to start a siloxane chain scission, a trifluoromethane sulfonic acid is used

preferably. Although especially the temperature requirement of a condensation reaction is not limited, it is preferably carried out by the 10 to 150 degrees C temperature requirement. Moreover, the polysiloxane which has two substituents which contain annular carbonate on each silicon of this invention is the general formula manufactured by method which was described above. [0028]

[Formula 19]

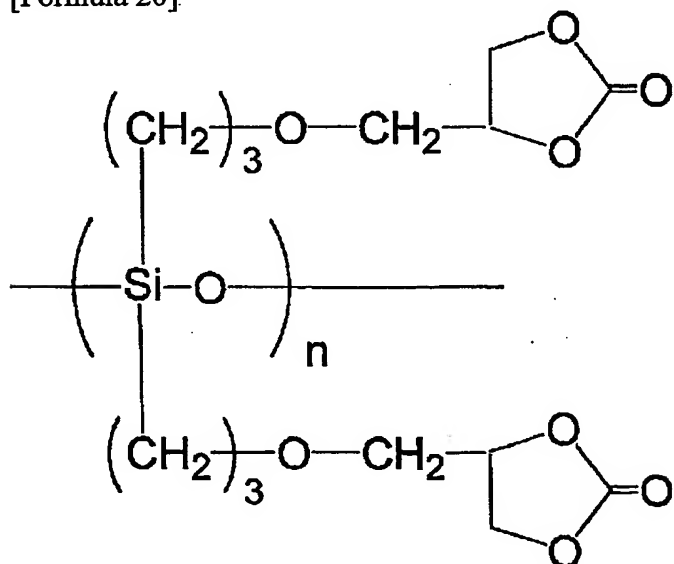


[0029] The dichlorosilane and the acid which are expressed with (the inside X1 and X2 of a formula being the substituent which has an annular carbonate machine, and being that X1 and X2 are of the same kind respectively or different species) are made to react under existence of an organic solvent. subsequently. Although especially the acid used here although a molecule end is made to generate the diorganopolysiloxane which has a silanol group by added and stirring water and a proton acid into the obtained reaction mixture is not limited, a hydrochloric acid etc. is mentioned preferably. The amount of the acid used usually has desirable 0.5 to 4.0 which is the amount which becomes 0.4-5.0 mols per one mol of above-mentioned dichlorosilane, and is the equivalent mols here. As for the organic solvent used for this invention, diethylether, an acetonitrile, a ketone, and an acetic-acid alkyl are mentioned. Although methyl acetate, ethyl acetate, an isopropyl acetate, n propyl acetate, an isobutyl acetate, etc. are illustrated and a methyl ethyl ketone, a methyl isobutyl ketone, etc. are illustrated as a ketone as an acetic-acid alkyl, a methyl ethyl ketone and a methyl isobutyl ketone are used preferably. Moreover, it is also possible to use other organic solvents together to these organic solvents. In this way, the polymerization of the polysiloxane which has a silanol group at the obtained chain end can be further carried out to the bottom of acid condensation catalyst existence. As an acid condensation catalyst, a concentrated sulfuric acid, a trifluoromethane sulfonic acid, dodecylbenzenesulfonic acid, etc. are illustrated. Moreover, what mixed 2-ethyl hexanoic acid with tetramethyl guanidine by this mol is effective. Since a condensation reaction is started at a room temperature and it is hard to start a siloxane chain scission, a trifluoromethane sulfonic acid is used preferably. Although especially the temperature requirement of a condensation reaction is not limited, it is preferably carried out by the 150-degree C temperature requirement from a room temperature. Although the example of a compound of this polysiloxane obtained by such method is shown, this invention is not limited to the following compounds. In addition, in compounds 1-6, n expresses one or more integers.

(Example 1 of a compound)

[0030]

[Formula 20]



TMA were doubled, and since [ if conversely low, ] it is disadvantageous as a industrial manufacturing method, a bird clapper is desirable [ especially the non-proton nature polar solvent used by this invention ] in 10 - 70% of the weight of the range. These are independent or are used combining two or more kinds.

[0031] As for the weight average molecular weight of (A) siloxane denaturation polyamidoimide resin of this invention, it is desirable that it is 30,000-100,000 from the balance of a property, and it is more desirable that it is 45,000-85,000. When there is an inclination for thermal resistance to fall [ this weight average molecular weight ] less than by 30,000 and 100,000 is exceeded, there is an inclination for an adhesive property to fall. In this invention, weight average molecular weight is measured using the calibration curve by standard polystyrene by the gel permeation chromatography method (GPC).

[0032] The non-aqueous-solvent system binder constituent of this invention can be made to contain (B) thermosetting resin if needed. As the above-mentioned thermosetting resin, an epoxy resin, phenol resin, polyester resin, polyimide resin, a bismaleimide triazine resin, etc. are mentioned, for example.

[0033] Especially the epoxy resin from the point of an adhesive property and handling nature is desirable. as the above-mentioned epoxy resin For example, the bisphenol A type epoxy resin, a bisphenol female mold epoxy resin, A bisphenol S type epoxy resin, a phenol novolak type epoxy resin, A cresol novolak type epoxy resin, a naphthalene type epoxy resin, and its denaturation object, BIKISHIRE nil diglycidyl ether, YDC1312 (Tohto Kasei make), TMH574 (Sumitomo Chemical make), Epicoat 1031S (product made from oil-ized shell), Aromatic system epoxy resins, such as EPOTOTO 8125 (tradename by Tohto Kasei Co., Ltd.), Neopentyl glycol diglycidyl ether, polypropylene glycol diglycidyl ether, Heterocycle formula epoxy compounds, such as aliphatic system epoxy resins, such as tetrahydrophthalic acid diglycidyl ester, and a triglycidyl isocyanate, EPOLEAD PB3600 (tradename made from Die Cell Chemistry), etc. are mentioned.

[0034] In these, it is desirable to use the epoxy resin which has two or more glycidyl groups, and its hardening accelerator. Moreover, a glycidyl group is so good that there are, and if it is three or more pieces, it is still more desirable. [ many ] Loadings change with number of glycidyl groups, and the loadings to a silicone denaturation polyamidoimide resin are so good that there are many glycidyl groups at least. Moreover, it is still more desirable if the curing agent of an epoxy resin is used together. These are independent or are used combining two or more kinds.

[0035] As for the loadings of the epoxy resin used by this invention, it is desirable that it is the 5 - 100 weight section to an adhesive property, flexibility, and a heat-resistant point to the (A) component 100 weight section, and it is more desirable that it is 10 - 50 weight section. When there is an inclination for electrolytic-solution-proof nature with these loadings sufficient in under 5 weight sections not to be obtained and the 100 weight sections are exceeded, there is an inclination for a sufficient adhesive property and sufficient flexibility not to be obtained.

[0036] As the curing agent or hardening accelerator of the aforementioned epoxy resin, in an epoxy resin, the thing which reacts, or hardening, if it is a promotion \*\*\*\*\* thing, what thing may be used, for example, amines, imidazole derivatives, polyfunctional phenols, and acid anhydrides will be mentioned. As the above-mentioned amines, a dicyandiamide, a diamino diphenylmethane, a guanylurea, etc. are mentioned, for example. As the above-mentioned imidazole derivatives, alkyl group substitution imidazoles, such as a 2-ethyl-4-methyl imidazole, a benzimidazole, etc. are mentioned, for example. As the above-mentioned polyfunctional phenols, novolak phenol type phenol resin, resole type phenol resin, etc. which are a hydroquinone, a resorcinol, bisphenol A and these halogenated compounds, and the addition condensation object of the aforementioned polyfunctional phenols and formaldehyde are mentioned, for example. As the above-mentioned acid anhydrides, phthalic anhydride, a benzophenone tetracarboxylic acid dihydrate, methyl himic acid, etc. are mentioned, for example. Among these, as a hardening accelerator, especially the thing for which imidazole derivatives are used is desirable.

[0037] In the case of amines, the initial complement of these curing agents or a hardening accelerator has the desirable amount to which the equivalent of the active hydrogen of an amine and the weight per epoxy equivalent of an epoxy resin become almost equal. In the case of an imidazole, it does not become equivalent ratio with active hydrogen simply, but it is [ 0.1 - 10.0 weight section ] experientially necessary to the epoxy resin 100 weight section. In the case of polyfunctional phenols, 0.6 to 1.2 hydroxyl equivalent is required to 1Eq of epoxy groups of an epoxy resin. Since a non-hardened epoxy resin remains if there are few amounts of these curing agents or a hardening accelerator, an adhesive property falls, and since an unreacted curing agent and an unreacted hardening accelerator remain if many [ too ], electrolytic-solution-proof nature falls. These are independent or are used combining two or more kinds.

[0038] In this invention, a non-aqueous solvent is made to dissolve or distribute these constituents so that a solid content may become about 10 - 30% of the weight, and it considers as a non-aqueous-solvent system binder constituent. As the above-mentioned non-aqueous solvent, if solubility is acquired, what thing may be used and a dimethylacetamide, a dimethylformamide, dimethyl sulfoxide, a N-methyl-2-pyrrolidone, gamma-butyrolactone, a sulfolane, a cyclohexanone, etc. will be mentioned, for example. These are independent or are used combining two or more kinds.

[0039] The non-aqueous-solvent system binder constituent and active material of this invention can be mixed, it can apply to an electrode base front face, and an electrode can be manufactured by removing a polar non-aqueous solvent. As the above-mentioned electrode base, aluminum, copper, etc. are mentioned, for example.

[0040] Although a well-known thing can be used as the above-mentioned active material, for example, the end of a carbon powder, such as an amorphous carbon and an artificial graphite, etc. is mentioned, it is desirable that it is the transition-metals oxide which can insert or emit a lithium ion in reversible, and lithium manganese multiple oxides, such as lithium nickel multiple oxides, such as lithium cobalt multiple oxides, such as a cobalt acid lithium, and a nickel acid lithium, and a manganic acid lithium, such mixture, etc. are mentioned as these examples, for example.

[0041] In the above-mentioned lithium nickel multiple oxide, the lithium nickel multiple oxide which replaced the nickel site or the lithium site with at least one or more sorts of metals chosen from aluminum, V, Cr, Fe, Co, Sr, Mo, W, Mn, B, Mg, etc. is sufficient. Also in the above-mentioned lithium manganese multiple oxide, the lithium manganese multiple oxide which replaced the manganese site or the lithium site with at least one or more sorts of metals chosen from Li, aluminum, V, Cr, Fe, Co, nickel, Mo, W, Zn, B, and Mg is sufficient.

[0042] As for the above-mentioned lithium manganese multiple oxide, it is desirable that it is  $\text{Li}_x\text{Mn}_y\text{O}_2$ . As for Above x, it is desirable that it is the range of  $0.2 \leq x \leq 2.5$ , and it is [ Above y ] desirable that it is  $0.8 \leq y \leq 1.25$ . The amount of Mn eluted from a positive active material since a non-aqueous-solvent system binder constituent exists so that a part of particle front face of a lithium manganese multiple oxide may be worn when manufacturing a non-aqueous-solvent system rechargeable battery, using the above-mentioned lithium manganese multiple oxide as a positive active material can be reduced, the electronic-conduction nature of a positive electrode is secured, and since degradation of the negative electrode by Mn eluted in one side can also be suppressed, the organic electrolytic-solution rechargeable battery which has improved the cell capacity fall by the charge-and-discharge cycle can obtain.

[0043] Although especially a limit does not have a non-aqueous-solvent system rechargeable battery using the above-mentioned electrode For example, it winds through the separator which consists of a polyethylene fine porous membrane etc. Produce a spiral-like winding group, insert this winding group in a cell can, and the nickel tab terminal beforehand welded to the copper foil of a negative-electrode charge collector is welded to a battery can bottom. The electrolytic solution is put into the obtained cell container, and the aluminum tab terminal beforehand welded to the aluminum foil of a positive-electrode charge collector is welded to a lid, and a lid can be arranged in the upper part of a cell can through an insulating gasket, and it can carry out sealing etc. and can manufacture.

[0044] As the above-mentioned electrolytic solution, for example, organic solvents, such as carbonate, ester, ether, ketones, lactone, nitril, amines, amides, sulfur compounds, chlorinated hydrocarbons, and sulfolane system compounds, are mentioned, and independent or two or more kinds of mixed solvents, such as propylene carbonate, ethylene carbonate, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, diethyl carbonate, gamma-butyrolactone, a tetrahydrofuran, diethylether, a sulfolane, an acetonitrile, dimethyl carbonate, and a N-methyl-2-pyrrolidone, are desirable As the above-mentioned electrolyte, LiClO<sub>4</sub>, LiPF<sub>6</sub>, LiPF<sub>4</sub>, LiBF<sub>4</sub>, LiCl, LiBr, CH<sub>3</sub>SO<sub>3</sub>Li, and LiAsF<sub>6</sub> grade are mentioned, for example.

[0045] The electrode of this invention is excellent in the adhesion of the binder layer containing an active material, and the metallic foil which is an electrode base, excellent in electrolytic-solution-proof nature and thermal resistance, and even if used under an elevated temperature, it can maintain an electrode base, a binder layer, and the adhesion intensity between binder layers for a long period of time. if an electrode base, a binder layer, and the adhesion intensity between binder layers improve -- a mixture -- the addition of an inner non-aqueous-solvent system binder constituent can be reduced, it is possible to, increase the amount of active materials as a result, and the cell using this electrode can increase a volume energy density Since the cell using the electrode which maintained an electrode base, a binder layer, and the adhesion intensity between binder layers for a long period of time can maintain an electrode base, a binder layer, and the electric conduction network between binder layers and can perform a charge reaction and an electric discharge reaction uniformly even if it repeats charge and discharge, its cycle-life property can also improve.

[0046]

[Example] Hereafter, this invention is explained in detail based on an example. In addition, unless it refuses especially among an example, the section and % show weight section and weight %, respectively.

[0047] (Composition of a siloxane conversion polyamidoimide resin) with [ which connected the reflux condenser ] a cock -- the 1l. separable flask equipped with the 25ml moisture fixed quantity receiver, the thermometer, and the stirrer -- as an aroma diamine as 2 and 2-screw [4-(4-amino phenoxy) phenyl] propane and a siloxane diamine -- reactant silicone-oil X-22-161- it taught with the compounding ratio which showed NMP (N-methyl-2-pyrrolidone) in Table 1, respectively as AS (the tradename by Shin-Etsu Chemical Co., Ltd., amine equivalent 416), TMA (trimellitic anhydride), and a non-proton nature polar solvent, and agitated for 30 minutes at 80 degrees C And after supplying 100ml of toluene as an aromatic hydrocarbon in which water and azeotropy are possible, temperature was raised and it was made to flow back at 160 degrees C for 2 hours. It checked that 3.6ml or more of water has collected on a moisture fixed quantity receiver, and that the outflow of water was no longer seen, and removing an effluent collected on the moisture fixed quantity receiver, temperature was raised to about 190 degrees C, and toluene was removed. Then, the solution was returned to the room temperature, the amount which showed MDI (4 and 4'-diphenylmethane diisocyanate) in Table 1 as aromatic diisocyanate was supplied, and it was made to react at 190 degrees C for 2 hours. The NMP solution of the siloxane conversion polyamidoimide resin A-1 and the siloxane conversion polyamidoimide resin A-2 was obtained after the reaction end.

[0048]

[Table 1]

表 1

試 料 名		A-1	A-2
配 合 (部)	BAPP <sup>-1</sup>	28.7	32.8
	X-22-161AS <sup>-2</sup>	58.3	16.6
	TMA <sup>-3</sup>	56.5	40.4
	NMP <sup>-4</sup>	383.6	307.3
	MDI <sup>-5</sup>	42.0	30.0

加 熱 残 分 (%)	32	26
重 量 平 均 分 子 量	63500	66000

- \*1: 2, 2-ビス[4-(4-アミノフェノキシ)フェニル]プロパン  
 \*2: 反応性シリコンオイル (信越化学工業株式会社製商品名)、  
 シロキサン系両末端アミン  
 \*3: 無水トリメリット酸  
 \*4: N-メチル-2-ピロリドン  
 \*5: 4, 4'-ジフェニルメタンジイソシアネート

[0049] (Production of a non-aqueous-solvent system binder constituent)

The material shown in Table 2 to examples 1-6, the siloxane conversion polyamidoimide resin A-1 obtained example of comparison 1, and the siloxane conversion polyamidoimide resin A-2 was added, and the constituent for binders was obtained. After applying the N-methyl-2-pyrrolidone solution (the product made from the Kureha chemistry, tradename KF-1100) of a polyvinylidene fluoride to rolling copper foil as obtained resin constituent I-VI for binders, and an example 1 of comparison so that it may become about 30 micrometers of dryness thickness, it dried at 120 degrees C for 3 hours, and dryness hardening was carried out at 180 degrees C for 2 hours, and the hardening paint film was obtained. Subsequently, the hardening paint film was stuck on the glass plate which stuck the double-sided tape beforehand, and the rolling copper foil adhesion hardening paint film stuck on the glass plate was obtained. The adhesive property (Peel intensity to rolling copper foil) of this hardening paint film was measured. The result was shown in Table 2.

[0050]

[Table 2]

表 2

(重量部)

試 料 名		実施例 1	実施例 2	実施例 3	実施例 4	実施例 5	実施例 6	比較例 1		
		非水溶媒系バインダ組成物						比較樹脂		
		I	II	III	IV	V	VI			
(A) 成 分	シロキサン変性アミドイミド樹脂 A-1 (固形分 32%)	313	313	313	313	313	—	—		
	シロキサン変性アミドイミド樹脂 A-2 (固形分 26%)	—	—	—	—	—	385	—		
	ポリフッ化ビニリデン樹脂 (固形分 12%)	—	—	—	—	—	—	833 (固形分 100)		
(B) 成 分	ビスフェノール A 型エポキシ : エポトート 8125 *6	40	50	60	50	50	50	—		
	エポキシ化ポリブタジエン : エポリード PB3600 *7	10	10	10	5	15	10	—		
	2-エチル-4-メチルイミダゾール	0.2	0.2	0.2	0.2	0.2	0.2	—		
接 着 性		ピール強度 (KN/m)		1	0.9	0.8	0.9	1.1	0.9	0.5

\*6: 東都化成株式会社商品名

\*7: ダイセル化学株式会社商品名

[0051] (Production of a negative-electrode electrode)

The amorphous carbon of 20 micrometers of example 7 mean particle diameters and the non-aqueous-solvent system binder constituent I are mixed at a rate of 96:4, injection mixture is carried out at a N-methyl-2-pyrrolidone, and a slurry-like solution is produced. This solution is applied to both sides of copper foil with a thickness of 10 micrometers, and it dries to them. a mixture -- a

coverage is one side 65 g/m<sup>2</sup> a mixture -- bulk density becomes 1.0 g/cm<sup>3</sup> -- as -- a roll-press machine -- rolling out -- 56mm width of face -- cutting -- a short \*\*-like negative electrode -- a mixture -- the electrode sheet was produced a negative electrode -- a mixture -- the current collection tab of the product [ edge / of an electrode sheet ] made from nickel -- ultrasonic welding -- carrying out -- a bridge formation of removal of the remains solvent in after that and an electrode, and the water of adsorption, and a non-aqueous-solvent system binder constituent sake -- 180 degrees C -- a 1-hour vacuum drying -- carrying out -- a negative electrode -- a mixture -- the electrode was obtained

[0052] The negative-electrode electrode was obtained like the example 7 except using non-aqueous-solvent system binder constituent II-VI at the time of production of the solution of the shape of an example 8 - 12 slurries.

[0053] The non-aqueous-solvent system binder constituent I is mixed with the artificial graphite of 20 micrometers of example 13 mean particle diameters at a rate of 95:5, injection mixture is carried out at a N-methyl-2-pyrrolidone, and a slurry-like solution is produced. This solution is applied to both sides of copper foil with a thickness of 10 micrometers, and it dries to them. a mixture -- a coverage is one side 65 g/m<sup>2</sup> a mixture -- bulk density becomes 1.0 g/cm<sup>3</sup> -- as -- a roll-press machine -- rolling out -- 56mm width of face -- cutting -- a short \*\*-like negative electrode -- a mixture -- the electrode sheet was produced a negative electrode -- a mixture -- the current collection tab of the product [ edge / of an electrode sheet ] made from nickel -- ultrasonic welding -- carrying out -- the bridge formation of removal and the resin constituent for non-aqueous-solvent system binders by the remains solvent in after that and an electrode, and adsorption sake -- 180 degrees C -- a 1-hour vacuum drying -- carrying out -- a negative electrode -- a mixture -- the electrode was obtained

[0054] The negative-electrode electrode was obtained like the example 13 except using non-aqueous-solvent system binder constituent II-VI at the time of production of the solution of the shape of an example 14 - 18 slurries.

[0055] Example of comparison 2 negative electrode mixes the amorphous carbon of 20 micrometers of mean particle diameters, and a polyvinylidene-fluoride resin at a rate of 90:10, carries out injection mixture at a N-methyl-2-pyrrolidone, and produces a slurry-like solution. This solution is applied to both sides of copper foil with a thickness of 10 micrometers, and it dries to them. a mixture -- a coverage is one side 65 g/m<sup>2</sup> a mixture -- bulk density becomes 1.0 g/cm<sup>3</sup> -- as -- a roll-press machine -- rolling out -- 56mm width of face -- cutting -- a short \*\*-like negative electrode -- a mixture -- the electrode sheet was produced a negative electrode -- a mixture -- the current collection tab of the product [ edge / of an electrode sheet ] made from nickel -- ultrasonic welding -- carrying out -- a heat curing of the remains solvent in after that and an electrode, or a removal of the water of adsorption and a binder resin sake -- 160 degrees C -- a 3-hour vacuum drying -- carrying out -- a negative electrode -- a mixture -- the electrode was obtained

[0056] The negative-electrode electrode was obtained like the example 13 except using a polyvinylidene-fluoride resin instead of an example of comparison 3 non-aqueous-solvent system binder constituent.

[0057] About the obtained electrode, electrolytic-solution-proof nature (existence of the abnormalities in appearance in one 1000 times the scale factor of this according to the electron microscope after being 24-hour immersed at 50 degrees C to these using the mixed liquor of the ethylene carbonate / dimethyl carbonate = 1/2 (volume ratio) in which LiPF<sub>6</sub> was dissolved as the electrolytic solution so that a N-methyl-2-pyrrolidone or concentration might be set to 1M) was evaluated. These results were shown in Table 3.

[0058]

[Table 3]



表 3

	使用した非水溶媒系バインダ組成物	電解液A *8	電解液B *9
実施例7	非水溶媒系バインダ組成物 I	外観異常なし	外観異常なし
実施例8	非水溶媒系バインダ組成物 II	外観異常なし	外観異常なし
実施例9	非水溶媒系バインダ組成物 III	外観異常なし	外観異常なし
実施例10	非水溶媒系バインダ組成物 IV	外観異常なし	外観異常なし
実施例11	非水溶媒系バインダ組成物 V	外観異常なし	外観異常なし
実施例12	非水溶媒系バインダ組成物 VI	外観異常なし	外観異常なし
実施例13	非水溶媒系バインダ組成物 I	外観異常なし	外観異常なし
実施例14	非水溶媒系バインダ組成物 II	外観異常なし	外観異常なし
実施例15	非水溶媒系バインダ組成物 III	外観異常なし	外観異常なし
実施例16	非水溶媒系バインダ組成物 IV	外観異常なし	外観異常なし
実施例17	非水溶媒系バインダ組成物 V	外観異常なし	外観異常なし
実施例18	非水溶媒系バインダ組成物 VI	外観異常なし	外観異常なし
比較例2	ポリフッ化ピリリデンのN-メチル-2-ピロリドン溶液 (呉羽化学製、商品名KF-1100)	表面膨潤	表面膨潤
比較例3	ポリフッ化ピリリデンのN-メチル-2-ピロリドン溶液 (呉羽化学製、商品名KF-1101)	表面膨潤	表面膨潤

\*8: 電解液A (濃度が1モル/リットルとなるようにLiPF<sub>6</sub>を溶解させたプロピレンカーボネートの混合液)

\*9: 電解液B (濃度が1モル/リットルとなるようにLiPF<sub>6</sub>を溶解させたエチレンカーボネート/ジメチルカーボネート=1/2 (体積比) の混合液)

[0059] the obtained negative electrode -- a mixture -- the charge and discharge test made to discharge until it results in neglect final-voltage 1V in discharge current 0.28 mA/cm<sup>2</sup>, after carrying out constant-potential charge of the charge capacity, service capacity, and irreversible capacity of the first time by the single electrode of an electrode by discharge current 0.28 mA/cm<sup>2</sup> and 5mV of discharge voltage was performed, and the cycle property was measured by repeating this The result was shown in Table 4 and 5.

[0060]

[Table 4]

表 4

	初 回		
	充電容量 (mAh/g)	放電容量 (mAh/g)	不可逆容量 (mAh/g)
実施例7	384	351	33
実施例8	387	354	33
実施例9	385	353	32
実施例10	386	354	32
実施例11	383	349	34
実施例12	380	345	35
実施例13	401	368	33

[0061]

[Table 5]



表 5

	初 回		
	充電容量 (mAh/g)	放電容量 (mAh/g)	不可逆容量 (mAh/g)
実施例14	405	370	35
実施例15	405	370	35
実施例16	400	367	33
実施例17	403	369	34
実施例18	395	360	35
比較例2	360	295	65
比較例3	370	300	70

[0062] (Production of a lithium secondary battery)

the scale-like natural graphite whose mean particle diameter is 1 micrometer as example 19 positive active material considering  $\text{LiCoO}_2$  as 89 % of the weight and an electric conduction agent -- 8 % of the weight and a binder -- carrying out -- the non-aqueous-solvent system binder resin constituent I -- 3 % of the weight -- adding -- this -- a N-methyl-2-pyrrolidone -- adding -- mixing -- a positive electrode -- the slurry of a mixture was adjusted the same -- as the negative-electrode matter -- as 95 % of the weight of amorphous carbons of 12 micrometers of mean particle diameters, and a binder -- the non-aqueous-solvent system binder resin constituent I -- 5 % of the weight -- adding -- this -- a N-methyl-2-pyrrolidone -- adding -- mixing -- a negative electrode -- the slurry of a mixture was obtained next, a positive electrode -- thickness applied the slurry of a mixture to both sides of the aluminum foil which is 25 micrometers, and carried out the vacuum drying at 120 degrees C after that for 1 hour After the vacuum drying, pressing of the electrode was carried out with the roller press, and thickness was set to 190 micrometers. The positive-electrode binder coverage per unit area was 49 mg/cm<sup>2</sup>, and width of face started it by 40mm in the size whose length is 285mm, and it produced the positive electrode. however, a portion with a length [ of the ends of a positive electrode ] of 10mm -- a positive electrode -- a mixture was not applied, but the aluminum foil was exposed, and the positive-electrode tab was stuck to one of these by pressure by ultrasonic jointing

[0063] on the other hand -- a negative electrode -- thickness applied the slurry of a mixture to both sides of the copper foil which is 10 micrometers, and carried out the vacuum drying at 120 degrees C after that for 1 hour After the vacuum drying, pressing of the electrode was carried out with the roller press, and thickness was set to 175 micrometers. The positive-electrode binder coverage per unit area was 20 mg/cm<sup>2</sup>, and width of face started it by 40mm in the size whose length is 290mm, and it produced the negative electrode. this -- a positive electrode -- the same -- a portion with a length [ of the ends of a negative electrode ] of 10mm -- a negative electrode -- a mixture was not applied, but copper foil was exposed, and the negative-electrode tab was stuck to one of these by pressure by ultrasonic jointing As for separator, thickness used the micropore film made from polyethylene whose width of face is 44mm by 25 micrometers.

[0064] Subsequently, it piled up in order of a positive electrode, separator, a negative electrode, and separator, this was wound, and it considered as the electrode group. This was inserted in the cell can of single 3 sizes, can bottom welding of the negative-electrode tab was carried out, and the converging section for closing a positive-electrode lid was formed. After pouring into a cell can the electrolytic solution which dissolved one mol /of 6 fluoride [ phosphoric-acid ] lithiums in the mixed solvent of the ethylene carbonate and diethyl carbonate of 1:1 l. by the volume ratio after this, the positive-electrode tab was welded to the positive-electrode lid, and the caulking lithium secondary battery was obtained for the positive-electrode lid after that.

[0065] The charge-and-discharge cycle property was evaluated using the obtained lithium secondary

battery. Charge of the produced lithium secondary battery was charged with constant-voltage current until current was set to 30mA by cell-voltage 4.2V, after charging by the constant current to cell-voltage 4.2V with 300mA of current. Electric discharge performed constant-current discharge until it was set to cell-voltage 2.8V with 300mA of current. This charge-and-discharge cycle was repeated 300 times. The service-capacity maintenance factor of the service capacity of 1 cycle eye, a 100 cycle eye, and a 300 cycle eye is shown in Table 6.

[0066] Except using resin II-IV for binders for the binder of 20 to example 24 positive electrode, and a negative electrode, the lithium secondary battery was produced like the example 19, and the charge-and-discharge cycle property was evaluated like the example 19. The service-capacity maintenance factor of the service capacity of 1 cycle eye, a 100 cycle eye, and a 300 cycle eye is shown in Table 6.

[0067] Except using the artificial graphite of 20 microns of mean particle diameters for an example 25 negative-electrode active material, the lithium secondary battery was produced like the example 19, and the charge-and-discharge cycle property was evaluated like the example 19. The service-capacity maintenance factor of the service capacity of 1 cycle eye, a 100 cycle eye, and a 300 cycle eye is shown in Table 6.

[0068] Except using resin II-IV for binders for the binder of 26 to example 30 positive electrode, and a negative electrode, the lithium secondary battery was produced like the example 25, and the charge-and-discharge cycle property was evaluated like the example 25. The service-capacity maintenance factor of the service capacity of 1 cycle eye, a 100 cycle eye, and a 300 cycle eye is shown in Table 6.

[0069] Except using a polyvinylidene-fluoride resin for the binder of example of comparison 4 positive electrode, and using a polyvinylidene fluoride for the binder of a negative electrode 10% of the weight 5% of the weight, the lithium secondary battery was produced like the example 19, and the charge-and-discharge cycle property was evaluated like the example 19. The service-capacity maintenance factor of the service-capacity 100 cycle eye of 1 cycle eye and a 300 cycle eye is shown in Table 6.

[0070] Except using a polyvinylidene fluoride for the binder of example of comparison 5 positive electrode, and using a polyvinylidene fluoride for the binder of a negative electrode 10% of the weight 5% of the weight, the lithium secondary battery was produced like the example 25, and the charge-and-discharge cycle property was evaluated like the example 25. The service-capacity maintenance factor of the service capacity of 1 cycle eye, a 100 cycle eye, and a 300 cycle eye is shown in Table 6.

[0071]

[Table 6]

表 6

試料名	正極活物質	負極活物質	正・負極結着剤	1サイクル目放電容量 (mAh)	100サイクル目放電容量維持率 (%)	300サイクル目放電容量維持率 (%)
実施例 19	LiCoO <sub>2</sub>	非晶質炭素	非水溶媒系バイ ンダ組成物 I	532	93	89
実施例 20	LiCoO <sub>2</sub>	非晶質炭素	非水溶媒系バイ ンダ組成物 II	535	93	88
実施例 21	LiCoO <sub>2</sub>	非晶質炭素	非水溶媒系バイ ンダ組成物 III	536	94	89
実施例 22	LiCoO <sub>2</sub>	非晶質炭素	非水溶媒系バイ ンダ組成物 IV	538	95	90
実施例 23	LiCoO <sub>2</sub>	非晶質炭素	非水溶媒系バイ ンダ組成物 V	533	93	89
実施例 24	LiCoO <sub>2</sub>	非晶質炭素	非水溶媒系バイ ンダ組成物 VI	535	94	90
比較例 4	LiCoO <sub>2</sub>	非晶質炭素	ポリフッ化ビニ リデン樹脂	420	88	76
実施例 25	LiCoO <sub>2</sub>	人造黒鉛	非水溶媒系バイ ンダ組成物 I	620	89	83
実施例 26	LiCoO <sub>2</sub>	人造黒鉛	非水溶媒系バイ ンダ組成物 II	623	88	84
実施例 27	LiCoO <sub>2</sub>	人造黒鉛	非水溶媒系バイ ンダ組成物 III	625	88	83
実施例 28	LiCoO <sub>2</sub>	人造黒鉛	非水溶媒系バイ ンダ組成物 IV	630	90	85

実施例 29	LiCoO <sub>2</sub>	人造黒鉛	非水溶媒系バイ ンダ組成物 V	615	87	82
実施例 30	LiCoO <sub>2</sub>	人造黒鉛	非水溶媒系バイ ンダ組成物 VI	625	88	84
比較例 5	LiCoO <sub>2</sub>	人造黒鉛	ポリフッ化ビニ リデン樹脂	510	65	21

[0072]

[Effect of the Invention] A non-aqueous-solvent system binder constituent according to claim 1 is excellent in an adhesive property, flexibility, and electrolytic-solution-proof nature, and very useful to the electrode of a non-aqueous-solvent system rechargeable battery. In addition to an effect of the invention according to claim 1, a non-aqueous-solvent system binder constituent according to claim 2 is further excellent in an adhesive property and thermal resistance, and very useful to the electrode of a non-aqueous-solvent system rechargeable battery. A non-aqueous-solvent system binder constituent according to claim 3 does so an effect of the invention according to claim 1 or 2, and thermal resistance is further excellent, and it is very useful to the electrode of a non-aqueous-solvent system rechargeable battery.

[0073] A non-aqueous-solvent system binder constituent according to claim 4 does so an effect of the invention according to claim 1, 2, or 3, and thermal resistance and electrolytic-solution-proof nature are further excellent, and it is very useful to the electrode of a non-aqueous-solvent system rechargeable battery. A non-aqueous-solvent system binder constituent according to claim 5 does so an effect of the invention according to claim 4, and thermal resistance and electrolytic-solution-proof nature are further excellent, and it is very useful to the electrode of a non-aqueous-solvent system rechargeable battery. The manufacturing method of an electrode according to claim 6 is excellent in the cycle-life property when making it an adhesive property, flexibility, electrolytic-solution-proof nature, and a cell, and the adhesive property under an elevated temperature, and very useful to a non-aqueous-solvent system rechargeable battery.

[0074] The manufacturing method of an electrode according to claim 7 does so an effect of the invention according to claim 6, and the cycle-life property when making it a cell further is excellent, and it is very useful to a non-aqueous-solvent system rechargeable battery. The manufacturing method of an electrode according to claim 8 does so an effect of the invention according to claim 7, and the cycle-life property when making it a cell further is excellent, and it is very useful to a non-aqueous-solvent system rechargeable battery.

[0075] An electrode according to claim 9 is excellent in the cycle-life property when making it an adhesive property, flexibility, electrolytic-solution-proof nature, and a cell, and the adhesive property under an elevated temperature, can be effective in increase in quantity of an active material, and can increase a volume energy density. The manufacturing method of a non-aqueous-solvent system rechargeable battery according to claim 10 is excellent in a cycle-life property, electrolytic-solution-proof nature, and the adhesive property under an elevated temperature, can be effective in increase in quantity of an active material, can increase a volume energy density, is small, and is high. [ of safety ] [ of burst / explosion danger ]

---

[Translation done.]

\* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation..

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

TECHNICAL FIELD

---

[The technical field to which invention belongs] this invention relates to a non-aqueous-solvent system binder constituent, the manufacturing method of an electrode, an electrode, and a non-aqueous-solvent system rechargeable battery.

---

[Translation done.]

## \* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

## PRIOR ART

---

[Description of the Prior Art] By progress of electronic technology, the performance of electronic equipment improves, small and portable-ization progress, and a cell of high-energy density is desired as a power supply. As a conventional rechargeable battery, although a lead accumulator, nickel, and a cadmium cell are mentioned, it is still inadequate in that a cell with a high energy density is obtained. Then, as what is replaced with these cells, the organic electrolytic-solution rechargeable battery (it is described as a lithium secondary battery below) of high-energy density is developed, and it has spread quickly.

[0003] After a carbon material with little fear of the deposit of flexibility and a lithium which occlusion discharge of a lithium was possible for and was excellent is used for a negative electrode in lithium compound metallic oxides, such as a lithium cobalt multiple oxide, in a positive electrode, and a lithium secondary battery carries out the double spread of what the N-methyl-2-pyrrolidone (NMP) was made to distribute these and a binder resin, and was made into the slurry on the metallic foil which is a charge collector and dries a solvent, it is pressed with a roller-press machine. Positive and the negative-electrode board have been obtained. Many polyvinylidene fluorides (PVDF) are mainly used as a binder.

[0004] However, since adhesion of the interface of a charge collector and a binder layer and the adhesion between binder layers are inferior when a polyvinylidene fluoride is used as a binder, at the time of manufacturing processes, such as a decision process, a winding process, etc. of a plate, some mixtures exfoliate and are omitted from a charge collector, and it becomes a very small short circuit and the cause of cell capacity dispersion. Moreover, in order to expand and contract especially the carbon material of a negative electrode by repeating charge and discharge, there was a problem that a mixture exfoliates and is omitted from a charge collector, or the ununiformity of decline in current collection efficiency and a reaction with a lithium arose, and cell capacity fell gradually by the fall of adhesion between mixtures.

[0005] The monomer and unsaturation dibasicity monoester which furthermore make the fluoride vinylidene of a publication a principal component at JP,6-172452,A are copolymerized. When using the obtained fluoride vinylidene system copolymer as a binder, although the adhesion intensity with a charge collector improved, the abnormal-temperature elevation under the high voltage decomposed, hydrogen fluoride was generated, and it reacted with the lithium intercalation compound (GIC) of a negative-electrode board front face, or the depositing metal lithium, carried out unusual generation of heat, and had a possibility that a cell might explode and explode.

[0006] The proposal which uses thermoplastics, such as polyimide resin given in synthetic rubber and JP,6-163031,A containing styrene-butadiene-rubber (SBR) system synthetic rubber given in JP,5-74461,A and diene system rubber given in JP,9-87571,A, as binders other than fluororesins, such as a polyvinylidene fluoride, is made. However, it dissolves to the electrolytic solution, or these are swollen greatly, and cannot maintain adhesion of the interface of a charge collector and a binder layer, and adhesion between binder layers for a long period of time. Moreover, in case the electrode which flexibility was low and produced is wound even if it forms a binder layer when using polyimide resin, the crack of a binder layer and ablation arise and capacity is reduced. Although it has electrolytic-solution-proof nature, uniform distribution of an active material, a binder, etc. is very difficult, a cellulose, a surfactant, etc. need to be added, these dissolve in the electrolytic solution, and diene system synthetic rubber, such as styrene butadiene rubber, reduces the charge-and-discharge

efficiency of a cell.

---

[Translation done.]

\* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

## EFFECT OF THE INVENTION

---

[Effect of the Invention] A non-aqueous-solvent system binder constituent according to claim 1 is excellent in an adhesive property, flexibility, and electrolytic-solution-proof nature, and very useful to the electrode of a non-aqueous-solvent system rechargeable battery. In addition to an effect of the invention according to claim 1, a non-aqueous-solvent system binder constituent according to claim 2 is further excellent in an adhesive property and thermal resistance, and very useful to the electrode of a non-aqueous-solvent system rechargeable battery. A non-aqueous-solvent system binder constituent according to claim 3 does so an effect of the invention according to claim 1 or 2, and thermal resistance is further excellent, and it is very useful to the electrode of a non-aqueous-solvent system rechargeable battery.

[0073] A non-aqueous-solvent system binder constituent according to claim 4 does so an effect of the invention according to claim 1, 2, or 3, and thermal resistance and electrolytic-solution-proof nature are further excellent, and it is very useful to the electrode of a non-aqueous-solvent system rechargeable battery. A non-aqueous-solvent system binder constituent according to claim 5 does so an effect of the invention according to claim 4, and thermal resistance and electrolytic-solution-proof nature are further excellent, and it is very useful to the electrode of a non-aqueous-solvent system rechargeable battery. The manufacturing method of an electrode according to claim 6 is excellent in the cycle-life property when making it an adhesive property, flexibility, electrolytic-solution-proof nature, and a cell, and the adhesive property under an elevated temperature, and very useful to a non-aqueous-solvent system rechargeable battery.

[0074] The manufacturing method of an electrode according to claim 7 does so an effect of the invention according to claim 6, and the cycle-life property when making it a cell further is excellent, and it is very useful to a non-aqueous-solvent system rechargeable battery. The manufacturing method of an electrode according to claim 8 does so an effect of the invention according to claim 7, and the cycle-life property when making it a cell further is excellent, and it is very useful to a non-aqueous-solvent system rechargeable battery.

[0075] An electrode according to claim 9 is excellent in the cycle-life property when making it an adhesive property, flexibility, electrolytic-solution-proof nature, and a cell, and the adhesive property under an elevated temperature, can be effective in increase in quantity of an active material, and can increase a volume energy density. The manufacturing method of a non-aqueous-solvent system rechargeable battery according to claim 10 is excellent in a cycle-life property, electrolytic-solution-proof nature, and the adhesive property under an elevated temperature, can be effective in increase in quantity of an active material, can increase a volume energy density, is small, and is high. [ of safety ] [ of rupture and explosion risk ]

---

[Translation done.]

## \* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation..

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

## TECHNICAL PROBLEM

---

[Problem(s) to be Solved by the Invention] Invention according to claim 1 is excellent in an adhesive property, flexibility, and electrolytic-solution-proof nature, and provides the electrode of a non-aqueous-solvent system rechargeable battery with a very useful non-aqueous-solvent system binder constituent. In addition to an effect of the invention according to claim 1, invention according to claim 2 is further excellent in an adhesive property and thermal resistance, and provides the electrode of a non-aqueous-solvent system rechargeable battery with a very useful non-aqueous-solvent system binder constituent. Invention according to claim 3 does so an effect of the invention according to claim 1 or 2, and thermal resistance is further excellent, and it provides the electrode of a non-aqueous-solvent system rechargeable battery with a very useful non-aqueous-solvent system binder constituent.

[0008] Invention according to claim 4 does so an effect of the invention according to claim 1, 2, or 3, and thermal resistance and electrolytic-solution-proof nature are further excellent, and it provides the electrode of a non-aqueous-solvent system rechargeable battery with a very useful non-aqueous-solvent system binder constituent. Invention according to claim 5 does so an effect of the invention according to claim 4, and thermal resistance and electrolytic-solution-proof nature are further excellent, and it provides the electrode of a non-aqueous-solvent system rechargeable battery with a very useful non-aqueous-solvent system binder constituent. Invention according to claim 6 is excellent in the cycle-life property when making it an adhesive property, flexibility, electrolytic-solution-proof nature, and a cell, and the adhesive property under an elevated temperature, and provides a non-aqueous-solvent system rechargeable battery with the manufacturing method of a very useful electrode.

[0009] invention according to claim 7 does so an effect of the invention according to claim 6, and the cycle-life property when making it a cell further is excellent, and it provides a non-aqueous-solvent \*\* rechargeable battery with the manufacturing method of a very useful electrode invention according to claim 8 does so an effect of the invention according to claim 7, and the cycle-life property when making it a cell further is excellent, and it provides a non-aqueous-solvent \*\* rechargeable battery with the manufacturing method of a very useful electrode

[0010] Invention according to claim 9 is excellent in the cycle-life property when making it an adhesive property, flexibility, electrolytic-solution-proof nature, and a cell, and the adhesive property under an elevated temperature, is effective in increase in quantity of an active material, and offers the electrode which can increase a volume energy density. Invention according to claim 10 is excellent in a cycle-life property, electrolytic-solution-proof nature, and the adhesive property under an elevated temperature, it can be effective in increase in quantity of an active material, and a volume energy density can be increased, burst / explosion danger is small and safety offers the manufacturing method of a high non-aqueous-solvent system rechargeable battery.

---

[Translation done.]



## \* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

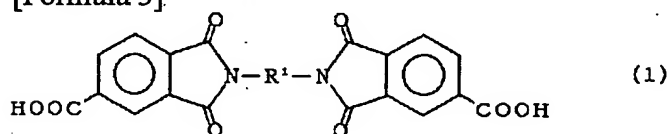
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## MEANS

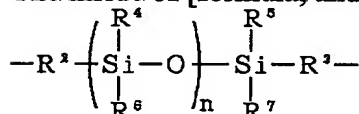
[Means for Solving the Problem] this invention relates to the non-aqueous-solvent system binder constituent which made the non-aqueous solvent dissolve or distribute (A) siloxane denaturation polyamidoimide resin. Moreover, this invention relates to the aforementioned non-aqueous-solvent system binder constituent whose siloxane denaturation polyamidoimide resin of the (A) component is a siloxane denaturation polyamidoimide resin which mixture, a multiple-valued carboxylic acid, or diisocyanate with a siloxane diamine, an aromatic diamine, or an aliphatic diamine is made to react, and is obtained.

[0012] Moreover, this invention is a general formula (1) from which the siloxane denaturation polyamidoimide resin of the (A) component makes mixture and trimellitic anhydride with a siloxane diamine, an aromatic diamine, or an aliphatic diamine react, and is obtained.

[Formula 3]



The inside of [formula, and R1. [Formula 4]



(-- the inside of a formula, and R2 and R3 -- each -- an independently divalent organic machine -- being shown -- R4, R5, R6, and R7 -- each -- the alkyl group of carbon numbers 1-20 and the aryl group of carbon numbers 6-18 are shown independently, and n is the integer of 1-50 -- it is related with the aforementioned non-aqueous-solvent system binder constituent which is the siloxane denaturation polyamidoimide resin which diisocyanate is made to react to the reactant containing the diimide dicarboxylic acid shown

[0013] Moreover, this invention relates to the aforementioned non-aqueous-solvent system binder constituent which made the non-aqueous solvent dissolve or distribute (B) thermosetting resin further. Moreover, this invention relates to the aforementioned non-aqueous-solvent system binder constituent whose thermosetting resin of the (B) component is an epoxy resin which has two or more glycidyl groups. Moreover, this invention mixes the aforementioned non-aqueous-solvent system binder constituent and an active material, and relates to the manufacturing method of the electrode characterized by removing a non-aqueous solvent after applying to an electrode base front face.

[0014] Moreover, this invention relates to the manufacturing method of the aforementioned electrode whose active material is the transition-metals oxide which can insert or emit a lithium ion in reversible by charge and discharge. Moreover, this invention relates to the manufacturing method of the aforementioned electrode which is the lithium manganese multiple oxide a transition-metals oxide is indicated to be by the general formula  $\text{Li}_x\text{M}_y\text{O}_2$  (the range of x is  $0.2 \leq x \leq 2.5$ , and the range of y is  $0.8 \leq y \leq 1.25$ ).

[0015] Moreover, this invention relates to the electrode manufactured according to the manufacturing method of the aforementioned electrode. Moreover, this invention relates to the non-aqueous-solvent

system rechargeable battery which used the aforementioned electrode for one [ at least ] pole of a non-aqueous-solvent system rechargeable battery.

[0016]

[Embodiments of the Invention] The non-aqueous-solvent system binder constituent of this invention needs to make a non-aqueous solvent dissolve or distribute (A) siloxane denaturation polyamidoimide resin.

[0017] The mole ratio of the number of sum total mols of the mixture (\*\*/\*\*=50/50 - 100 / 0 mole ratios) of for example, \*\* siloxane diamine, \*\* aromatic diamine, or an aliphatic diamine, a multiple-valued carboxylic acid, or diisocyanate can make the siloxane denaturation polyamidoimide resin (above-mentioned [ A ]) able to react by 1 / 2.20 - 1/2.05, and can obtain it. As for the mole ratio of the above-mentioned \*\*/\*\*, it is desirable that it is 50 / 50 - 100/0, and it is more desirable that it is 70 / 30 - 100/0. There is an inclination for an adhesive property to fall [ this mole ratio ] less than by 50/50.

[0018] As for the mole ratio of the number of sum total mols of the mixture of the aforementioned \*\* siloxane diamine, \*\* aromatic diamine, or an aliphatic diamine, a multiple-valued carboxylic acid, or diisocyanate, it is desirable that it is 1 / 2.20 - 1/2.05, and it is more desirable that it is 1 / 2.15 - 1/2.10. When there is an inclination for an adhesive property to fall [ this mole ratio ] less than by 1/2.20 and 1/2.05 is exceeded, there is an inclination for thermal resistance to fall.

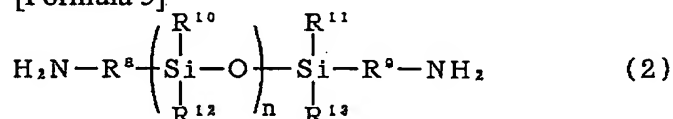
[0019] Moreover, as for the siloxane denaturation polyamidoimide resin (aforementioned [ A ]), it is desirable that it is the siloxane denaturation polyamidoimide resin which diisocyanate is made to react to the reactant containing the diimide dicarboxylic acid shown by the general formula (1) which mixture and trimellitic anhydride with a siloxane diamine, an aromatic diamine, or an aliphatic diamine are made to react, and is obtained, and is obtained.

[0020] As a divalent organic machine, arylene machines, such as alkylene machines, such as a methylene group, an ethylene, and a propylene machine, a phenylene group, a tolylene machine, and a xylylene machine, etc. are mentioned among the aforementioned general formula (1), for example. As an alkyl group of carbon numbers 1-20, among the aforementioned general formula (1) For example, a methyl group, an ethyl group, n-propyl group, an isopropyl machine, n-butyl, An isobutyl machine, a sec-butyl, a tert-butyl, a pentyl machine, An isopentyl machine, a neopentyl machine, a hexyl machine, a heptyl machine, an octyl machine, A nonyl machine, a decyl group, a undecyl machine, the dodecyl, a tridecyl machine, a tetradecyl machine, a pentadecyl group, a hexadecyl machine, a heptadecyl machine, an octadecyl machine, a nona decyl group, icosyl groups, these structural isomers, etc. are mentioned. Among the aforementioned general formula (1), as an aryl group of carbon numbers 6-18, a phenyl group, a tolyl group, a xylyl group, a biphenyl machine, a naphthyl group, an anthryl machine, a phenan tolyl group, etc. may be mentioned, and it may be replaced by a halogen atom, the amino group, a nitro group, the cyano group, the sulfhydryl group, the allyl group, the alkyl group of carbon numbers 1-20, etc., for example.

[0021] As for the mole ratio of the siloxane diamine for obtaining the diimide dicarboxylic acid shown by the aforementioned general formula (1), and trimellitic anhydride, it is desirable that it is 1 / 2.20 - 1/2.05, and it is more desirable that it is 1 / 2.15 - 1/2.10. Subsequently, the diimide dicarboxylic acid and diisocyanate which are shown by the aforementioned general formula (1) are made to react by the mole ratio 1 / 1.50 - 1/1.05, things are desirable, and it is more desirable to make it react by 1 / 1.35 - 1/1.20.

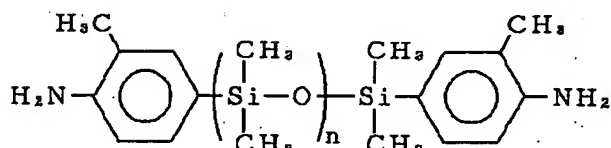
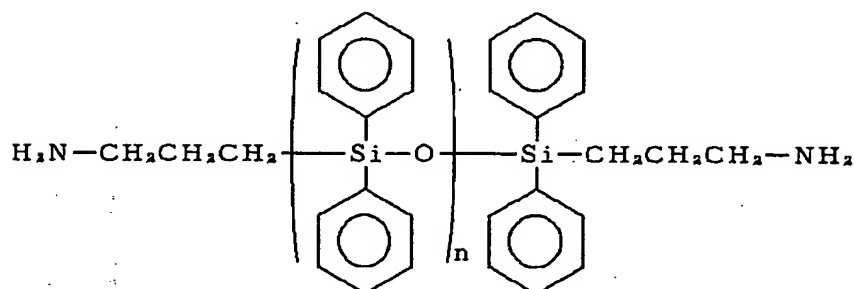
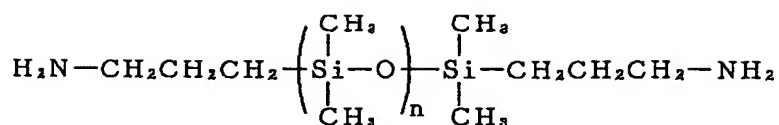
[0022] As the aforementioned siloxane diamine, it is a general formula (2), for example.

[Formula 5]



What is expressed with (R8 and R9 show a divalent organic machine independently respectively among a formula, R10, R11, R12, and R13 show the alkyl group of carbon numbers 1-20 and the aryl group of carbon numbers 6-18 independently respectively, and n is the integer of 1-50) is used.

[0023] As such a siloxane diamine, it is the following formula. [Formula 6]



What is shown for the (inside of a formula and n to be the integers) of 1-50 is mentioned.

[0024] Amino denaturation silicone-oil X-22-161AS which is a siloxane system both-ends amine also in these as an available thing commercially, for example (the amine equivalent 450, tradename by Shin-Etsu Chemical Co., Ltd.), X-22-161A (the amine equivalent 840, tradename by Shin-Etsu Chemical Co., Ltd.), X-22-161B (the amine equivalent 1500, tradename by Shin-Etsu Chemical Co., Ltd.), BY 16-853 (the amine equivalent 650, Dow Corning Toray Silicone tradename), BY16-853B (the amine equivalent 2200, Dow Corning Toray Silicone tradename), etc. are mentioned. a siloxane diamine -- the inside of a diamine from the point of an adhesive property and flexibility -- more than 50 mol % -- using is desirable These are independent or are used combining two or more kinds.

[0025] As the aforementioned aromatic diamine, for example O-phenylenediamine, m-phenylenediamine, p-phenylene diamine, 3, and 3'-diamino diphenyl-ether, 4, and 4'-diamino diphenyl-ether, 3, 4'-diamino diphenyl-ether, 3, and 3'-diamino diphenyl difluoromethane, 4, A 4'-diamino diphenyl fluoro methane, 3, and 3'-diaminodiphenyl-sulfone, 3, 4'-diaminodiphenyl-sulfone, 4, and 4'-diaminodiphenyl-sulfone, 3, and 3'-diamino diphenyl sulfide, 3, a 4'-diamino diphenyl sulfide, 4, 4'-diamino diphenyl sulfide, 3, and 3'-diamino diphenyl-ketone, 3, 4'-diamino diphenyl-ketone, 4, and 4'-diamino diphenyl SURUKETON, 2, and 2-screw (3-aminophenyl) propane, 2, and 2-(3, 4'-diamino diphenyl) propane, 2 and 2-Hexafluoro propane, 2, and 2-screw (4-aminophenyl) hexafluoro propane, 1, 3-screw (3-amino phenoxy) benzene 1, 4-screw (4-amino phenoxy) benzene, 3, 3'-[1, 4-phenylene screw (3, 4'-diamino diphenyl) ] screw aniline, 3, 4'-[1 and 4-phenylene screw (1-methyl ethylidene)] screw aniline, 4, and 4'-[1 and 4-phenylene screw (1-methyl ethylidene)] screw aniline, 2, and 2-screw [4- (1-methyl ethylidene) A phenyl] propane, 2, (3-amino phenoxy) 2-screw [4- Phenyl] propane, 2, and 2-screw [4-(3-amino phenoxy) phenyl] hexafluoro propane, 2, and 2-screw [4-(4-amino phenoxy) phenyl] hexafluoro propane, screw [4- (4-amino phenoxy) (3-amino phenoxy) A phenyl] sulfide, a screw [4-(3-amino phenoxy) phenyl] sulfone, a screw [4-(4-amino phenoxy) phenyl] sulfone, etc. are mentioned. It is desirable that it is what has three or more aromatic rings also in these. These are independent or are used combining two or more kinds.

[0026] As the aforementioned aliphatic diamine, there are an alkylene diamine, a polyoxyalkylene diamine, etc., for example. Moreover, heterocycle formula diamines, such as alicyclic diamines [, such as isophorone diamine, 4 and 4'-dicyclohexyl methanediamine, ], 3, and 9-screw (3-aminopropyl)-SUPIRO [ 2, 4, 8, and 10-tetrapod ] [5, 5] undecane, etc. are mentioned. These are independent or are used combining two or more kinds. As for the ratio of an aromatic diamine and an aliphatic diamine, it is desirable to use from a heat-resistant point at 20 or less % of the weight to the total quantity of an aromatic diamine / aliphatic diamine.

[0027] As the aforementioned multiple-valued carboxylic acid, for example Oxalic acid, a malonic acid, a succinic acid, A glutaric acid, an adipic acid, a pimelic acid, an azelaic acid, a sebacic acid,

ARUKIRENTE-Tell joint content dicarboxylic acids, such as dodecane 2 acid and eicosane 2 acid, Aliphatic dicarboxylic acids, such as an alkylene carbonate joint content dicarboxylic acid and a butadiene joint content dicarboxylic acid, Aromatic dicarboxylic acids, such as a phthalic acid, an isophthalic acid, a terephthalic acid, and a naphthalene dicarboxylic acid, Butane - 1, 2, 4-tricarboxylic acid, naphthalene - 1, 2, 4-tricarboxylic acid, Tricarboxylic acids, such as trimellitic acid, butane - 1, 2, 3, 4-tetracarboxylic acid, Pyromellitic acid, benzophenone -3, 3', 4, and 4'-tetracarboxylic acid, Tricarboxylic acids, such as diphenyl-ether -3, 3', 4, and 4'-tetracarboxylic acid, Biphenyl -3, 3', 4, and 4'-tetracarboxylic acid, naphthalene [ - Carboxylic acids, such as 1, 2 5, and 8-tetracarboxylic acid, an anhydrous TORIMETTO acid etc. are mentioned. ] - 2, 3, 6, 7-tetracarboxylic acid, naphthalene - 1, 2, 4, 5-tetracarboxylic acid, naphthalene As for an aliphatic dicarboxylic acid, it is desirable to use less than [ 20 mol % ] in a multiple-valued carboxylic acid from a heat-resistant point. These are independent or are used combining two or more kinds.

[0028] As the aforementioned aromatic diisocyanate, for example 4 and 4'-diphenylmethane diisocyanate (It abbreviates to MDI hereafter), 2, 4-tolylene diisocyanate, 2, 6-tolylene diisocyanate, 1, 5-naphthalene diisocyanate, tolidine di-isocyanate, p-phenyl diisocyanate, 4-4'-diphenyletherdiisocyanate, Aromatic diisocyanate, such as m-xylylene diisocyanate and m-tetramethyl xylylene diisocyanate, 1, 6-hexamethylene di-isocyanate, 2 and 2, 4-trimethylhexamethylene JIISHI cyanate, Cycloaliphatic diisocyanate, such as aliphatic diisocyanate [ , such as 2, 4, and 4-trimethylhexamethylene JIISHI cyanate, ], isophorone diisocyanate, 4, and 4'-dicyclohexylmethane diisocyanate, etc. is mentioned. As for aliphatic diisocyanate, it is desirable to use less than [ 10 mol % ] from a heat-resistant point. These are independent or are used combining two or more kinds.

[0029] The siloxane denaturation polyamidoimide resin of the (A) component used by this invention For example, mixture ((I)/(II) = 0.1/99.9 - 99.9 / 0.1 mole ratios) and trimellitic anhydride of an aromatic diamine or an aliphatic diamine (I), and a siloxane diamine (II) The number of sum total mols of ((I) + (II)) and the mole ratio of TMA (it abbreviates to TMA hereafter) by 1 / 2.20 - 1/2.05 under existence of a non-proton nature polar solvent Make it react at about 50-90 degrees C for about 0.2 to 1.5 hours, and the aromatic hydrocarbon in which water and azeotropy are still more possible is supplied by about 0.1 - 0.5% of the weight of the non-proton nature polar solvent. React at 120-180 degrees C, and the mixture containing siloxane diimide dicarboxylic acid is manufactured. This and aromatic diisocyanate (III) can be manufactured at reacting at about 150-250 degrees C for about 0.5 to 3 hours ((III) = 1/1.50 - 1 / 1.05 mole ratios) ((I) + (II)). Moreover, after manufacturing aromatic diimide dicarboxylic acid, an aromatic hydrocarbon can be removed from the solution by making the solution into about 150-250 degrees C, and it can also manufacture by performing the reaction of this and aromatic diisocyanate. Moreover, as for a siloxane denaturation polyamidoimide resin, it is desirable that it is a varnish containing a non-proton nature polar solvent.

[0030] It is desirable that they are a siloxane diamine and TMA, and the organic solvent that does not react as the aforementioned non-proton nature polar solvent, for example, in order to mention a dimethylacetamide, a dimethylformamide, dimethyl sulfoxide, a N-methyl-2-pyrrolidone, gamma-butyrolactone, a sulfolane, a cyclohexanone, etc. and for an imide-ized reaction to take an elevated temperature, especially a N-methyl-2-pyrrolidone with the high boiling point is desirable. Since a reaction does not fully advance but the moisture content contained in the above-mentioned non-proton nature polar solvent causes [ of a polymer ] a molecular weight fall by the trimellitic acid which TMA hydrates and generates, it is desirable to be managed at 0.2 or less % of the weight. Moreover, although not restricted, that the solubility of TMA falls and it becomes impossible to perform sufficient reaction when there are many rates of a weight with which a siloxane diamine and TMA were doubled, and since it is conversely disadvantageous as a low and a industrial manufacturing method, a bird clapper is desirable [ especially the non-proton nature polar solvent used by this invention ] in 10 - 70% of the weight of the range. These are independent or are used combining two or more kinds.

[0031] As for the weight average molecular weight of (A) siloxane denaturation polyamidoimide resin of this invention, it is desirable that it is 30,000-100,000 from the balance of a property, and it is more desirable that it is 45,000-85,000. When there is an inclination for thermal resistance to fall

[ this weight average molecular weight ] less than by 30,000 and 100,000 is exceeded, there is an inclination for an adhesive property to fall. In this invention, weight average molecular weight is measured using the calibration curve by standard polystyrene by the gel permeation chromatography method (GPC).

[0032] The non-aqueous-solvent system binder constituent of this invention can be made to contain (B) thermosetting resin if needed. As the above-mentioned thermosetting resin, an epoxy resin, phenol resin, polyester resin, polyimide resin, a bismaleimide triazine resin, etc. are mentioned, for example.

[0033] Especially the epoxy resin from the point of an adhesive property and handling nature is desirable. as the above-mentioned epoxy resin For example, the bisphenol A type epoxy resin, a bisphenol female mold epoxy resin, A bisphenol S type epoxy resin, a phenol novolak type epoxy resin, A cresol novolak type epoxy resin, a naphthalene type epoxy resin, and its denaturation object, BIKISHIRE nil diglycidyl ether, YDC1312 (Tohto Kasei make), TMH574 (Sumitomo Chemical make), Epicoat 1031S (product made from oil-ized shell), Aromatic system epoxy resins, such as EPOTOTO 8125 (tradename by Tohto Kasei Co., Ltd.), Neopentyl glycol diglycidyl ether, polypropylene glycol diglycidyl ether, Heterocycle formula epoxy compounds, such as aliphatic system epoxy resins, such as tetrahydrophtal acid diglycidyl ester, and a triglycidyl isocyanate, EPOLEAD PB3600 (tradename made from Die Cell Chemistry), etc. are mentioned.

[0034] In these, it is desirable to use the epoxy resin which has two or more glycidyl groups, and its hardening accelerator. Moreover, a glycidyl group is so good that there are, and if it is three or more pieces, it is still more desirable. [ many. ] Loadings change with number of glycidyl groups, and the loadings to a silicone denaturation polyamidoimide resin are so good that there are many glycidyl groups at least. Moreover, it is still more desirable if the curing agent of an epoxy resin is used together. These are independent or are used combining two or more kinds.

[0035] As for the loadings of the epoxy resin used by this invention, it is desirable that it is the 5 - 100 weight section to an adhesive property, flexibility, and a heat-resistant point to the (A) component 100 weight section, and it is more desirable that it is 10 - 50 weight section. When there is an inclination for electrolytic-solution-proof nature with these loadings sufficient in under 5 weight sections not to be obtained and the 100 weight sections are exceeded, there is an inclination for a sufficient adhesive property and sufficient flexibility not to be obtained.

[0036] As the curing agent or hardening accelerator of the aforementioned epoxy resin, in an epoxy resin, the thing which reacts, or hardening, if it is a promotion \*\*\*\*\* thing, what thing may be used, for example, amines, imidazole derivatives, polyfunctional phenols, and acid anhydrides will be mentioned. As the above-mentioned amines, a dicyandiamide, a diamino diphenylmethane, a guanylurea, etc. are mentioned, for example. As the above-mentioned imidazole derivatives, alkyl group substitution imidazoles, such as a 2-ethyl-4-methyl imidazole, a benzimidazole, etc. are mentioned, for example. As the above-mentioned polyfunctional phenols, novolak phenol type phenol resin, resol type phenol resin, etc. which are a hydroquinone, a resorcinol, bisphenol A and these halogenated compounds, and the addition condensation object of the aforementioned polyfunctional phenols and formaldehyde are mentioned, for example. As the above-mentioned acid anhydrides, phthalic anhydride, a benzophenone tetracarboxylic acid dihydrate, methyl himic acid, etc. are mentioned, for example. Among these, as a hardening accelerator, especially the thing for which imidazole derivatives are used is desirable.

[0037] In the case of amines, the initial complement of these curing agents or a hardening accelerator has the desirable amount to which the equivalent of the active hydrogen of an amine and the weight per epoxy equivalent of an epoxy resin become almost equal. In the case of an imidazole, it does not become equivalent ratio with active hydrogen simply, but it is [ 0.1 - 10.0 weight section ] experientially necessary to the epoxy resin 100 weight section. In the case of polyfunctional phenols, 0.6 to 1.2 hydroxyl equivalent is required to 1Eq of epoxy groups of an epoxy resin. Since a non-hardened epoxy resin remains if there are few amounts of these curing agents or a hardening accelerator, an adhesive property falls, and since an unreacted curing agent and an unreacted hardening accelerator remain if many [ too ], electrolytic-solution-proof nature falls. These are independent or are used combining two or more kinds.

[0038] In this invention, a non-aqueous solvent is made to dissolve or distribute these constituents so that a solid content may become about 10 - 30% of the weight, and it considers as a non-aqueous-solvent system binder constituent. As the above-mentioned non-aqueous solvent, if solubility is acquired, what thing may be used and a dimethylacetamide, a dimethylformamide, dimethyl sulfoxide, a N-methyl-2-pyrrolidone, gamma-butyrolactone, a sulfolane, a cyclohexanone, etc. will be mentioned, for example. These are independent or are used combining two or more kinds.

[0039] The non-aqueous-solvent system binder constituent and active material of this invention can be mixed, it can apply to an electrode base front face, and an electrode can be manufactured by removing a polar non-aqueous solvent. As the above-mentioned electrode base, aluminum, copper, etc. are mentioned, for example.

[0040] Although a well-known thing can be used as the above-mentioned active material, for example, the end of a carbon powder, such as an amorphous carbon and an artificial graphite, etc. is mentioned, it is desirable that it is the transition-metals oxide which can insert or emit a lithium ion in reversible, and lithium manganese multiple oxides, such as lithium nickel multiple oxides, such as lithium cobalt multiple oxides, such as a cobalt acid lithium, and a nickel acid lithium, and a manganic acid lithium, such mixture, etc. are mentioned as these examples, for example.

[0041] In the above-mentioned lithium nickel multiple oxide, the lithium nickel multiple oxide which replaced the nickel site or the lithium site with at least one or more sorts of metals chosen from aluminum, V, Cr, Fe, Co, Sr, Mo, W, Mn, B, Mg, etc. is sufficient. Also in the above-mentioned lithium manganese multiple oxide, the lithium manganese multiple oxide which replaced the manganese site or the lithium site with at least one or more sorts of metals chosen from Li, aluminum, V, Cr, Fe, Co, nickel, Mo, W, Zn, B, and Mg is sufficient.

[0042] As for the above-mentioned lithium manganese multiple oxide, it is desirable that it is  $\text{Li}_x\text{Mn}_y\text{O}_2$ . As for Above x, it is desirable that it is the range of  $0.2 \leq x \leq 2.5$ , and it is [ Above y ] desirable that it is  $0.8 \leq y \leq 1.25$ . The amount of Mn eluted from a positive active material since a non-aqueous-solvent system binder constituent exists so that a part of particle front face of a lithium manganese multiple oxide may be worn when manufacturing a non-aqueous-solvent system rechargeable battery, using the above-mentioned lithium manganese multiple oxide as a positive active material can be reduced, the electronic-conduction nature of a positive electrode is secured, and since degradation of the negative electrode by Mn eluted in one side can also be suppressed, the organic electrolytic-solution rechargeable battery which has improved the cell capacity fall by the charge-and-discharge cycle can obtain.

[0043] Although especially a limit does not have a non-aqueous-solvent system rechargeable battery using the above-mentioned electrode For example, it winds through the separator which consists of a polyethylene fine porous membrane etc. Produce a spiral-like winding group, insert this winding group in a cell can, and the nickel tab terminal beforehand welded to the copper foil of a negative-electrode charge collector is welded to a battery can bottome. The electrolytic solution is put into the obtained cell container, and the aluminum tab terminal beforehand welded to the aluminum foil of a positive-electrode charge collector is welded to a lid, and a lid can be arranged in the upper part of a cell can through an insulating gasket, and it can carry out sealing etc. and can manufacture.

[0044] As the above-mentioned electrolytic solution, for example, organic solvents, such as carbonate, ester, ether, ketones, lactone, nitril, amines, amides, sulfur compounds, chlorinated hydrocarbons, and sulfolane system compounds, are mentioned, and independent or two or more kinds of mixed solvents, such as propylene carbonate, ethylene carbonate, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, diethyl carbonate, gamma-butyrolactone, a tetrahydrofuran, diethylether, a sulfolane, an acetonitrile, dimethyl carbonate, and a N-methyl-2-pyrrolidone, are desirable As the above-mentioned electrolyte,  $\text{LiClO}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiPF}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiCl}$ ,  $\text{LiBr}$ ,  $\text{CH}_3\text{SO}_3\text{Li}$ , and  $\text{LiAsF}_6$  grade are mentioned, for example.

[0045] The electrode of this invention is excellent in the adhesion of the binder layer containing an active material, and the metallic foil which is an electrode base, excellent in electrolytic-solution-proof nature and thermal resistance, and even if used under an elevated temperature, it can maintain an electrode base, a binder layer, and the adhesion intensity between binder layers for a long period of time. if an electrode base, a binder layer, and the adhesion intensity between binder layers improve --

a mixture -- the addition of an inner non-aqueous-solvent system binder constituent can be reduced, it is possible to, increase the amount of active materials as a result, and the cell using this electrode can increase a volume energy density. Since the cell using the electrode which maintained an electrode base, a binder layer, and the adhesion intensity between binder layers for a long period of time can maintain an electrode base, a binder layer, and the electric conduction network between binder layers and can perform a charge reaction and an electric discharge reaction uniformly even if it repeats charge and discharge, its cycle-life property can also improve.

---

[Translation done.]



## \* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## EXAMPLE

[Example] Hereafter, this invention is explained in detail based on an example. In addition, unless it refuses especially among an example, the section and % show weight section and weight %, respectively.

[0047] (Composition of a siloxane conversion polyamidoimide resin) with [ which connected the reflux condenser ] a cock -- the 1l. separable flask equipped with the 25ml moisture fixed quantity receiver, the thermometer, and the stirrer -- as an aroma diamine as 2 and 2-screw [4-(4-amino phenoxy) phenyl] propane and a siloxane diamine -- reactant silicone-oil X-22-161- it taught with the compounding ratio which showed NMP (N-methyl-2-pyrrolidone) in Table 1, respectively as AS (the tradename by Shin-Etsu Chemical Co., Ltd., amine equivalent 416), TMA (trimellitic anhydride), and a non-proton nature polar solvent, and agitated for 30 minutes at 80 degrees C. And after supplying 100ml of toluene as an aromatic hydrocarbon in which water and azeotropy are possible, temperature was raised and it was made to flow back at 160 degrees C for 2 hours. It checked that 3.6ml or more of water has collected on a moisture fixed quantity receiver, and that the outflow of water was no longer seen, and removing an effluent collected on the moisture fixed quantity receiver, temperature was raised to about 190 degrees C, and toluene was removed. Then, the solution was returned to the room temperature, the amount which showed MDI (4 and 4'-diphenylmethane diisocyanate) in Table 1 as aromatic diisocyanate was supplied, and it was made to react at 190 degrees C for 2 hours. The NMP solution of the siloxane conversion polyamidoimide resin A-1 and the siloxane conversion polyamidoimide resin A-2 was obtained after the reaction end.

[0048]

[Table 1]

表 1

試 料 名		A-1	A-2
配 合 (部)	BAPP <sup>*1</sup>	28.7	32.8
	X-22-161AS <sup>*2</sup>	58.3	16.6
	TMA <sup>*3</sup>	56.5	40.4
	NMP <sup>*4</sup>	383.6	307.3
	MDI <sup>*5</sup>	42.0	30.0
加 熱 残 分 (%)		32	26
重 量 平 均 分 子 量		63500	66000

- \*1: 2, 2-ビス [4-(4-アミノフェノキシ) フェニル] プロパン  
 \*2: 反応性シリコンオイル (信越化学工業株式会社製商品名)、  
 シロキサン系両末端アミン  
 \*3: 無水トリメリット酸  
 \*4: N-メチル-2-ピロリドン  
 \*5: 4, 4'-ジフェニルメタンジイソシアネート

[0049] (Production of a non-aqueous-solvent system binder constituent)

The material shown in Table 2 to examples 1-6, the siloxane conversion polyamidoimide resin A-1, obtained example of comparison 1, and the siloxane conversion polyamidoimide resin A-2 was added, and the constituent for binders was obtained. After applying the N-methyl-2-pyrrolidone solution (the product made from the Kureha chemistry, tradename KF-1100) of a polyvinylidene

[http://www4.ipdl.jpo.go.jp/cgi-bin/tran\\_web.cgi\\_ejje](http://www4.ipdl.jpo.go.jp/cgi-bin/tran_web.cgi_ejje)



fluoride to rolling copper foil as obtained resin constituent I-VI for binders, and an example 1 of comparison so that it may become about 30 micrometers of dryness thickness, it dried at 120 degrees C for 3 hours, and dryness hardening was carried out at 180 degrees C for 2 hours, and the hardening paint film was obtained. Subsequently, the hardening paint film was stuck on the glass plate which stuck the double-sided tape beforehand, and the rolling copper foil adhesion hardening paint film stuck on the glass plate was obtained. The adhesive property (Peel intensity to rolling copper foil) of this hardening paint film was measured. The result was shown in Table 2.

[0050]

[Table 2]

		表 2						(重量部)
試 料 名		実施例 1	実施例 2	実施例 3	実施例 4	実施例 5	実施例 6	比較例 1
		非水溶媒系バインダ組成物						比較樹脂
		I	II	III	IV	V	VI	
(A) 成 分	シロキサン変性アミドイミド樹脂 A-1 (固形分 32%)	313	313	313	313	313	—	—
	シロキサン変性アミドイミド樹脂 A-2 (固形分 26%)	—	—	—	—	—	385	—
	ポリフッ化ピリデン樹脂 (固形分 12%)	—	—	—	—	—	—	833 (固形分 100)
(B) 成 分	ビスフェノール A 型エポキシ : エポトート 8125 *6	40	50	60	50	50	50	—
	エポキシ化ポリブタジエン : エポリード PB3600 *7	10	10	10	5	15	10	—
	2-エチル-4-メチルイミダゾール	0.2	0.2	0.2	0.2	0.2	0.2	—
接 着 性		ピール強度 (KN/m)						0.5

\*6: 東都化成株式会社商品名

\*7: ダイセル化学株式会社商品名

[0051] (Production of a negative-electrode electrode)

The amorphous carbon of 20 micrometers of example 7 mean particle diameters and the non-aqueous-solvent system binder constituent I are mixed at a rate of 96:4, injection mixture is carried out at a N-methyl-2-pyrrolidone, and a slurry-like solution is produced. This solution is applied to both sides of copper foil with a thickness of 10 micrometers, and it dries to them. a mixture -- a coverage is one side 65 g/m<sup>2</sup> a mixture -- bulk density becomes 1.0 g/cm<sup>3</sup> -- as -- a roll-press machine -- rolling out -- 56mm width of face -- cutting -- a short \*\*-like negative electrode -- a mixture -- the electrode sheet was produced a negative electrode -- a mixture -- the current collection tab of the product [ edge / of an electrode sheet ] made from nickel -- ultrasonic welding -- carrying out -- a bridge formation of removal of the remains solvent in after that and an electrode, and the water of adsorption, and a non-aqueous-solvent system binder constituent sake -- 180 degrees C -- a 1-hour vacuum drying -- carrying out -- a negative electrode -- a mixture -- the electrode was obtained

[0052] The negative-electrode electrode was obtained like the example 7 except using non-aqueous-solvent system binder constituent II-VI at the time of production of the solution of the shape of an example 8 - 12 slurries.

[0053] The non-aqueous-solvent system binder constituent I is mixed with the artificial graphite of 20 micrometers of example 13 mean particle diameters at a rate of 95:5, injection mixture is carried out at a N-methyl-2-pyrrolidone, and a slurry-like solution is produced. This solution is applied to both sides of copper foil with a thickness of 10 micrometers, and it dries to them. a mixture -- a coverage is one side 65 g/m<sup>2</sup> a mixture -- bulk density becomes 1.0 g/cm<sup>3</sup> -- as -- a roll-press machine -- rolling out -- 56mm width of face -- cutting -- a short \*\*-like negative electrode -- a mixture -- the

electrode sheet was produced a negative electrode -- a mixture -- the current collection tab of the product [ edge / of an electrode sheet ] made from nickel -- ultrasonic welding -- carrying out -- the bridge formation of removal and the resin constituent for non-aqueous-solvent system binders by the remains solvent in after that and an electrode, and adsorption sake -- 180 degrees C -- a 1-hour vacuum drying -- carrying out -- a negative electrode -- a mixture -- the electrode was obtained [0054] The negative-electrode electrode was obtained like the example 13 except using non-aqueous-solvent system binder constituent II-VI at the time of production of the solution of the shape of an example 14 - 18 slurries.

[0055] Example of comparison 2 negative electrode mixes the amorphous carbon of 20 micrometers of mean particle diameters, and a polyvinylidene-fluoride resin at a rate of 90:10, carries out injection mixture at a N-methyl-2-pyrrolidone, and produces a slurry-like solution. This solution is applied to both sides of copper foil with a thickness of 10 micrometers, and it dries to them. a mixture -- a coverage is one side 65 g/m<sup>2</sup> a mixture -- bulk density becomes 1.0 g/cm<sup>3</sup> -- as -- a roll-press machine -- rolling out -- 56mm width of face -- cutting -- a short \*\*-like negative electrode -- a mixture -- the electrode sheet was produced a negative electrode -- a mixture -- the current collection tab of the product [ edge / of an electrode sheet ] made from nickel -- ultrasonic welding -- carrying out -- a heat curing of the remains solvent in after that and an electrode, or a removal of the water of adsorption and a binder resin sake -- 160 degrees C -- a 3-hour vacuum drying -- carrying out -- a negative electrode -- a mixture -- the electrode was obtained

[0056] The negative-electrode electrode was obtained like the example 13 except using a polyvinylidene-fluoride resin instead of an example of comparison 3 non-aqueous-solvent system binder constituent.

[0057] About the obtained electrode, electrolytic-solution-proof nature (existence of the abnormalities in appearance in one 1000 times the scale factor of this according to the electron microscope after being 24-hour immersed at 50 degrees C to these using the mixed liquor of the ethylene carbonate / dimethyl carbonate = 1/2 (volume ratio) in which LiPF<sub>6</sub> was dissolved as the electrolytic solution so that a N-methyl-2-pyrrolidone or concentration might be set to 1M) was evaluated. These results were shown in Table 3.

[0058]

[Table 3]

表 3

	使用した非水溶媒系バインダ組成物	電解液 A *8	電解液 B *9
実施例 7	非水溶媒系バインダ組成物 I	外観異常なし	外観異常なし
実施例 8	非水溶媒系バインダ組成物 II	外観異常なし	外観異常なし
実施例 9	非水溶媒系バインダ組成物 III	外観異常なし	外観異常なし
実施例 10	非水溶媒系バインダ組成物 IV	外観異常なし	外観異常なし
実施例 11	非水溶媒系バインダ組成物 V	外観異常なし	外観異常なし
実施例 12	非水溶媒系バインダ組成物 VI	外観異常なし	外観異常なし
実施例 13	非水溶媒系バインダ組成物 I	外観異常なし	外観異常なし
実施例 14	非水溶媒系バインダ組成物 II	外観異常なし	外観異常なし
実施例 15	非水溶媒系バインダ組成物 III	外観異常なし	外観異常なし
実施例 16	非水溶媒系バインダ組成物 IV	外観異常なし	外観異常なし
実施例 17	非水溶媒系バインダ組成物 V	外観異常なし	外観異常なし
実施例 18	非水溶媒系バインダ組成物 VI	外観異常なし	外観異常なし
比較例 2	ポリフッ化ピニリデンのN-メチル-2-ピロリドン溶液 (呉羽化学製、商品名KF-1100)	表面膨潤	表面膨潤
比較例 3	ポリフッ化ピニリデンのN-メチル-2-ピロリドン溶液 (呉羽化学製、商品名KF-1101)	表面膨潤	表面膨潤

\*8: 電解液A (濃度が1モル/リットルとなるようにLiPF<sub>6</sub>を溶解させたプロピレンカーボネートの混合液)

\*9: 電解液B (濃度が1モル/リットルとなるようにLiPF<sub>6</sub>を溶解させたエチレンカーボネート/ジメチルカーボネート=1/2 (体積比) の混合液)

[0059] the obtained negative electrode -- a mixture -- the charge and discharge test made to discharge

until it results in neglect final-voltage 1V in discharge current 0.28 mA/cm<sup>2</sup>, after carrying out constant-potential charge of the charge capacity, service capacity, and irreversible capacity of the first time by the single electrode of an electrode by discharge current 0.28 mA/cm<sup>2</sup> and 5mV of discharge voltage was performed, and the cycle property was measured by repeating this The result was shown in Table 4 and 5.

[0060]

[Table 4]

表 4

	初 回		
	充電容量 (mAh/g)	放電容量 (mAh/g)	不可逆容量 (mAh/g)
実施例 7	384	351	33
実施例 8	387	354	33
実施例 9	385	353	32
実施例 10	386	354	32
実施例 11	383	349	34
実施例 12	380	345	35
実施例 13	401	368	33

[0061]

[Table 5]

表 5

	初 回		
	充電容量 (mAh/g)	放電容量 (mAh/g)	不可逆容量 (mAh/g)
実施例 14	405	370	35
実施例 15	405	370	35
実施例 16	400	367	33
実施例 17	403	369	34
実施例 18	395	360	35
比較例 2	360	295	65
比較例 3	370	300	70

[0062] (Production of a lithium secondary battery)

the scale-like natural graphite whose mean particle diameter is 1 micrometer as example 19 positive active material considering LiCoO<sub>2</sub> as 89 % of the weight and an electric conduction agent -- 8 % of the weight and a binder -- carrying out -- the non-aqueous-solvent system binder resin constituent I -- 3 % of the weight -- adding -- this -- a N-methyl-2-pyrrolidone -- adding -- mixing -- a positive electrode -- the slurry of a mixture was adjusted the same -- as the negative-electrode matter -- as 95 % of the weight of amorphous carbons of 12 micrometers of mean particle diameters, and a binder -- the non-aqueous-solvent system binder resin constituent I -- 5 % of the weight -- adding -- this -- a N-methyl-2-pyrrolidone -- adding -- mixing -- a negative electrode -- the slurry of a mixture was obtained next, a positive electrode -- thickness applied the slurry of a mixture to both sides of the aluminum foil which is 25 micrometers, and carried out the vacuum drying at 120 degrees C after that for 1 hour After the vacuum drying, pressing of the electrode was carried out with the roller press, and thickness was set to 190 micrometers. The positive-electrode binder coverage per unit area was 49 mg/cm<sup>2</sup>, and width of face started it by 40mm in the size whose length is 285mm, and it produced the positive electrode. however, a portion with a length [ of the ends of a positive electrode ] of 10mm -- a positive electrode -- a mixture was not applied, but the aluminum foil was exposed, and the positive-electrode tab was stuck to one of these by pressure by ultrasonic jointing

[0063] on the other hand -- a negative electrode -- thickness applied the slurry of a mixture to both

sides of the copper foil which is 10 micrometers, and carried out the vacuum drying at 120 degrees C after that for 1 hour. After the vacuum drying, pressing of the electrode was carried out with the roller press, and thickness was set to 175 micrometers. The positive-electrode binder coverage per unit area was 20 mg/cm<sup>2</sup>, and width of face started it by 40mm in the size whose length is 290mm, and it produced the negative electrode. this -- a positive electrode -- the same -- a portion with a length [ of the ends of a negative electrode ] of 10mm -- a negative electrode -- a mixture was not applied, but copper foil was exposed, and the negative-electrode tab was stuck to one of these by pressure by ultrasonic jointing. As for separator, thickness used the micropore film made from polyethylene whose width of face is 44mm by 25 micrometers.

[0064] Subsequently, it piled up in order of a positive electrode, separator, a negative electrode, and separator, this was wound, and it considered as the electrode group. This was inserted in the cell can of single 3 sizes, can bottom welding of the negative-electrode tab was carried out, and the converging section for closing a positive-electrode lid was formed. After pouring into a cell can the electrolytic solution which dissolved one mol /of 6 fluoride [ phosphoric-acid ] lithiums in the mixed solvent of the ethylene carbonate and diethyl carbonate of 1:1 l. by the volume ratio after this, the positive-electrode tab was welded to the positive-electrode lid, and the caulking lithium secondary battery was obtained for the positive-electrode lid after that.

[0065] The charge-and-discharge cycle property was evaluated using the obtained lithium secondary battery. Charge of the produced lithium secondary battery was charged with constant-voltage current until current was set to 30mA by cell-voltage 4.2V, after charging by the constant current to cell-voltage 4.2V with 300mA of current. Electric discharge performed constant-current discharge until it was set to cell-voltage 2.8V with 300mA of current. This charge-and-discharge cycle was repeated 300 times. The service-capacity maintenance factor of the service capacity of 1 cycle eye, a 100 cycle eye, and a 300 cycle eye is shown in Table 6.

[0066] Except using resin II-IV for binders for the binder of 20 to example 24 positive electrode, and a negative electrode, the lithium secondary battery was produced like the example 19, and the charge-and-discharge cycle property was evaluated like the example 19. The service-capacity maintenance factor of the service capacity of 1 cycle eye, a 100 cycle eye, and a 300 cycle eye is shown in Table 6.

[0067] Except using the artificial graphite of 20 microns of mean particle diameters for an example 25 negative-electrode active material, the lithium secondary battery was produced like the example 19, and the charge-and-discharge cycle property was evaluated like the example 19. The service-capacity maintenance factor of the service capacity of 1 cycle eye, a 100 cycle eye, and a 300 cycle eye is shown in Table 6.

[0068] Except using resin II-IV for binders for the binder of 26 to example 30 positive electrode, and a negative electrode, the lithium secondary battery was produced like the example 25, and the charge-and-discharge cycle property was evaluated like the example 25. The service-capacity maintenance factor of the service capacity of 1 cycle eye, a 100 cycle eye, and a 300 cycle eye is shown in Table 6.

[0069] Except using a polyvinylidene-fluoride resin for the binder of example of comparison 4 positive electrode, and using a polyvinylidene fluoride for the binder of a negative electrode 10% of the weight 5% of the weight, the lithium secondary battery was produced like the example 19, and the charge-and-discharge cycle property was evaluated like the example 19. The service-capacity maintenance factor of the service-capacity 100 cycle eye of 1 cycle eye and a 300 cycle eye is shown in Table 6.

[0070] Except using a polyvinylidene fluoride for the binder of example of comparison 5 positive electrode, and using a polyvinylidene fluoride for the binder of a negative electrode 10% of the weight 5% of the weight, the lithium secondary battery was produced like the example 25, and the charge-and-discharge cycle property was evaluated like the example 25. The service-capacity maintenance factor of the service capacity of 1 cycle eye, a 100 cycle eye, and a 300 cycle eye is shown in Table 6.

[0071]

[Table 6]

表 6

試料名	正極活物質	負極活物質	正・負極結着剤	1サイクル目 放電容量 (mAh)	100サイクル目放電 容量維持率 (%)	300サイクル目放電 容量維持率 (%)
実施例19	$\text{LiCoO}_2$	非晶質炭素	非水溶媒系パイ ンダ組成物 I	532	93	89
実施例20	$\text{LiCoO}_2$	非晶質炭素	非水溶媒系パイ ンダ組成物 II	535	93	88
実施例21	$\text{LiCoO}_2$	非晶質炭素	非水溶媒系パイ ンダ組成物 III	536	94	89
実施例22	$\text{LiCoO}_2$	非晶質炭素	非水溶媒系パイ ンダ組成物 IV	538	95	90
実施例23	$\text{LiCoO}_2$	非晶質炭素	非水溶媒系パイ ンダ組成物 V	533	93	89
実施例24	$\text{LiCoO}_2$	非晶質炭素	非水溶媒系パイ ンダ組成物 VI	535	94	90
比較例4	$\text{LiCoO}_2$	非晶質炭素	ポリフッ化ビニ リデン樹脂	420	88	76
実施例25	$\text{LiCoO}_2$	人造黒鉛	非水溶媒系パイ ンダ組成物 I	620	89	83
実施例26	$\text{LiCoO}_2$	人造黒鉛	非水溶媒系パイ ンダ組成物 II	623	88	84
実施例27	$\text{LiCoO}_2$	人造黒鉛	非水溶媒系パイ ンダ組成物 III	625	88	83
実施例28	$\text{LiCoO}_2$	人造黒鉛	非水溶媒系パイ ンダ組成物 IV	630	90	85
実施例29	$\text{LiCoO}_2$	人造黒鉛	非水溶媒系パイ ンダ組成物 V	615	87	82
実施例30	$\text{LiCoO}_2$	人造黒鉛	非水溶媒系パイ ンダ組成物 VI	625	88	84
比較例5	$\text{LiCoO}_2$	人造黒鉛	ポリフッ化ビニ リデン樹脂	510	65	21

[Translation done.]

**THIS PAGE BLANK (USPTO)**